EFFECT OF LOW DENSITY

INERT GAS FLUSH

ON OXYGEN-COLUMBIUM REACTION

AT 1500°F to 2000°F

Contract NASw-722

FINAL REPORT

May 14, 1964

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1.0   INTRODUCTION AND SUMMARY

1.0 INTRODUCTION AND SUMMARY

Testing or processing of materials requires the surrounding atmosphere to have particular characteristics. The type of characteristics governs the type of environment. At times, the environment should have absolutely no effect and at other times have a very strong effect on the materials used. The environment must be inert in order to perform long term tests of materials for space applications. However, the reduction of iron oxides on stainless steel is generally performed in pure hydrogen at atmospheric pressure. Here the hydrogen has a strong effect on the chemical composition of the surface metal.

The work described in this report attempts to give an understanding to the mechanics of a new process. This process involves the use of a controlled flowing atmosphere to provide a container with the desired environment. The highest purity gas will be obtained by making a proper choice of pressure and gas velocity in the sample region. The superiority of this process over standard techniques is the ability to achieve wide ranges of impurity pressures at a minimum of gas flow and equipment cost.

The effect of total gas pressure can be seen in Fig. 1.1. A gas is processed to obtain an impurity concentration of 10 PPM. At one atmosphere total pressure, the impurity level is 7.6 (10^{-3}) torr. By reducing the total pressure of the gas three decades, the impurity pressure becomes 7.6 (10^{-6}) torr. (Equivalent to 10 PPB). This reduction of total pressure can be done easily without the use of a complicated vacuum system and requires only an oil sealed mechanical pump.

The gas velocity is also important. As can be seen in Fig. 1.2, a purge gas is introduced in a container and flows outward to the exit. At the exit of the tube, there is a high contaminant gas concentration which is attempting to diffuse upstream. The higher the quantity of gas flowing, the harder it is

for the contaminant to flow upstream. An analytic expression was
derived for the situation where the purge gas has no impurities.
This expression was verified experimentally using a mass

$$\frac{c_o}{c_\ell} = e^{-\frac{Vx}{D}}$$ (See 2.0 Mathematical Analysis)

spectrometer. The mass spectrometer was capable of detecting 1 PPM.
A summary of the data is shown in Fig. 3.9. Table 2.1 contains a
list of values of D for various impurities in argon. It was found
that the worst contaminant for back diffusion, with the exception
of H_2, He, and Ne, was nitrogen. From a value of D, the desired
impurity concentration c_o, the impurity concentration c_ℓ at $x = 0$,
the required gas velocity and tube length can be calculated.

The sources of contaminant gases were studied, (See Fig. 1.3)
such factors as surface migration, container outgassing, and tube
outgassing were all investigated analytically. It was found that a
region of extremely high purity gas could be obtained, governed
mainly by the purity of the inlet gas and the total operating
pressure.

The problem of having an impurity in the gas stream, a high
impurity concentration at the tube exit, and an active material in
the sample region greatly complicated the problem. However, an
approximation for the impurity concentration is

$$\frac{c_o}{c_\ell} = \frac{\exp\left(-\frac{v\ell}{D}\right) - \frac{\alpha v}{kc_\ell}\left(1 - \exp\frac{-v\ell}{D}\right) + \exp\frac{-v\ell}{D}}{\exp\left(\frac{-v\ell}{D}\right) - 1 - \frac{v}{k}}$$

α = impurity concentration in purge gas

k = constant of proportionality depending on sticking
fraction, sample area, tube area

(meaning of other symbols are given previously (See 2.0)

The effect of an active material in the test region has an
interesting effect on the impurity concentration-gas velocity
diagram. The diagram has a definite minimum for sticking fractions

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greater than 0. To pick the exact velocity which will result in this minimum requires a knowledge of the sticking fraction. Generally this is not known.

The conservative approach is to design a system assuming that s = 0 and to consider the gettering action as a bonus.

Ina purged system, the impurity concentration can be reduced continuously by decreasing the purge gas pressure and increasing the velocity. There are theoretical limitations however. The gas velocity is limited to a subsonic value and when the pressure is reduced to the point where continuum flow ceases to exist the equations break down. The flow velocity is limited by an economical pump size. The pressure is limited to the point where the mean free path of the purge gas becomes within approximately 10% of the tube diameter (See Fig. 1.4).

A set of equations was developed to obtain the minimum velocity needed and still attain the required sample concentration. The required pressure can then be determined.

A furnace was constructed to test the system. (See Fig. 4.6) The following is a test of the parameters required for design of the pumping system.

1. System Geometry (What size is required?)

   Crucible tube diameter = .94"
   Crucible tube length to bottom of sample = 5"

2. Crucible operating temperature = 2000°F

3. Outgassing rate of system enclosure = $\dot{q}$ (torr-liter/cm^{2}sec.)
   Assumed to be zero since by proper operational procedures and choice of materials, most outgassing materials could be eliminated.

4. Purity of purge gas (PPM)

5. Required impurity concentration in work region, c_o equivalent 3.5 (10^8) (molecules/cm^3)

6. Sticking fraction of sample (assumed to be zero)

7. Impurity concentration at the tube exit, $c_\ell = 7.06\,(10^{+13})$ (molecules/cm^3)

From these values the optimum pressure and velocity were found to be 12 cfm and .214 torr.

Several columbium - 1% zirconium samples were mounted in the furnace and exposed to the resulting environment at 1500°F, 1750°F and 2000°F for periods of time of one to ten days. The contaminant level in the samples was compared to the amount gettered in a vacuum system at 1×10^{-7} torr. The results are favorable.

This process has been virtually untried in the area of vacuum metallurgy. However, the areas of application are manifold, limited only by the designer's imagination. A few examples follow.

HYDROGEN REDUCTION

Hydrogen will reduce the oxygen in an iron melt quite readily. However, after a hydrogen deoxidation, vacuum is required to remove any residual hydrogen left in the melt and to prevent reoxidation during the pouring of the melt. The disadvantages of the hydrogen reduction are the cost and hazards of the process. Use of the gas flush process can be made directly in the vacuum vessel at pressures where the hydrogen sorption is minimal. The hazards of hydrogen in an enclosed vessel is minimized when operated at pressures less than 40 torr. (Reported by Vogt and Robertshaw, "Explosions in Vessels Containing Hydrogen at Low Pressures", AVS Transactions, 1955).

SHORT TERM TESTING

Materials are often tested for short periods of time at high temperatures. Reactions of the metals with air requires the test be performed in an inert atmosphere. Dilution of the environment in a test container takes a long time and large quantities of gas. Vacuum pumps are used to reduce the time. The low contaminant levels require complicated vacuum systems. Again, the gas purge process could be the perfect compromise giving a pressure low enough to not require long dilution times and use of the flushing technique to minimize the vacuum system requirements.

LONG TERM TESTING

The process has been designed to be used for long term

environmental testing of refractory metals. Here the purity levels required are extremely stringent. People at NASA, Cleveland have found contamination effects on the basic properties of the columbium alloys at pressures lower than 10^{-8} torr. At present, the gas flush process has not demonstrated its capability of producing impurity levels in this range. We are limited by the purity of the purge gas and the ability to detect impurities. Impurity levels of less than 1 part per billion with a corresponding impurity detectability are required. At present, we are in the process of designing a system capable of these levels.

Three areas of application have been listed. There are many more possibilities such as glow discharge heating, local purification in welding operations, vacuum system purging, diffusion separation techniques and any other method where environment control is critical. It is intended that this report will suggest them so the process will be used.
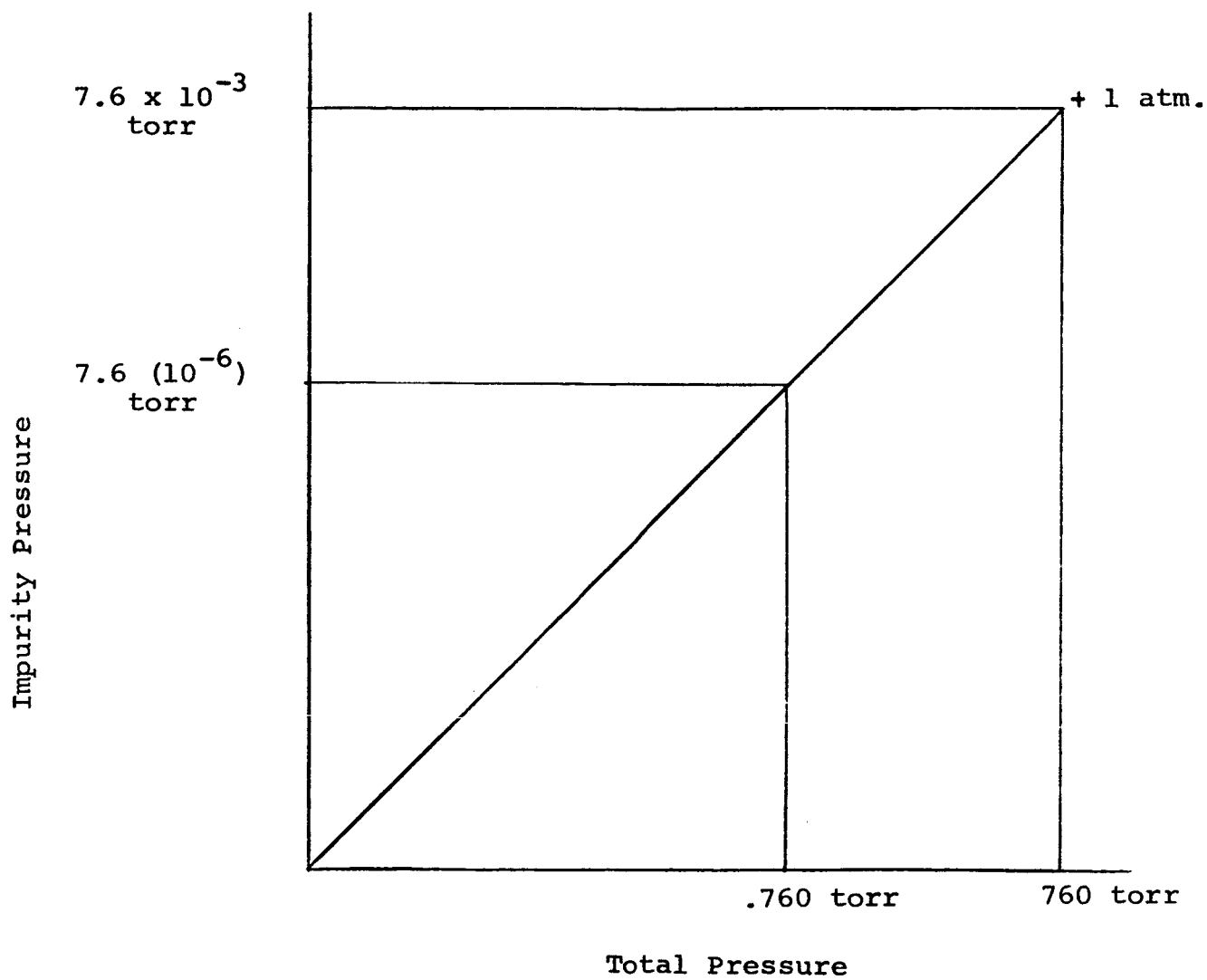
Effect of Pressure on Impurity Concentration

Figure 1.1

Purge gas velocity

Contaminant
Diffusion
Upstream

Purge Gas
Inlet

Sample
Area

V

c_ℓ

Contaminant
Concentration

$x = \ell$

$x = 0$
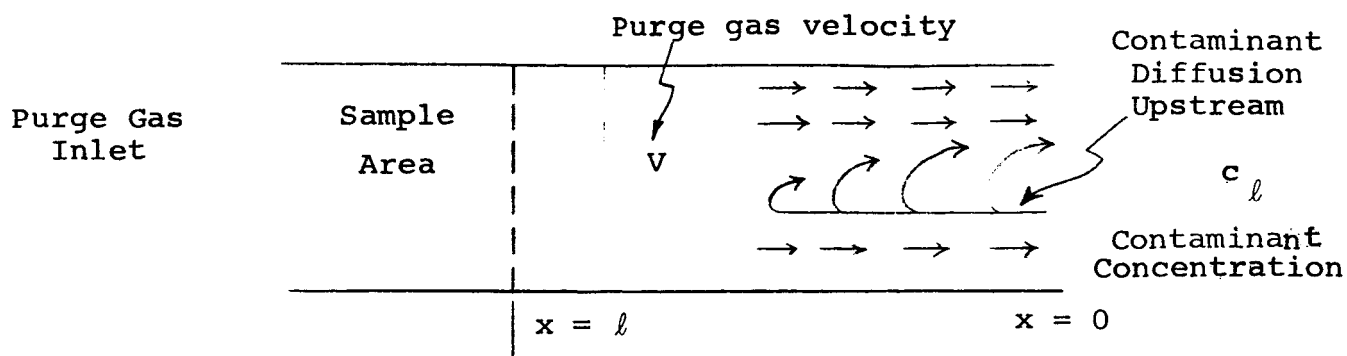
Effect of Gas Velocity

Figure   1.2

Surface Migration

Outgassing in Tube

Container
Outgassing

c_ℓ

Contaminant
Concentration
at Tube Exit
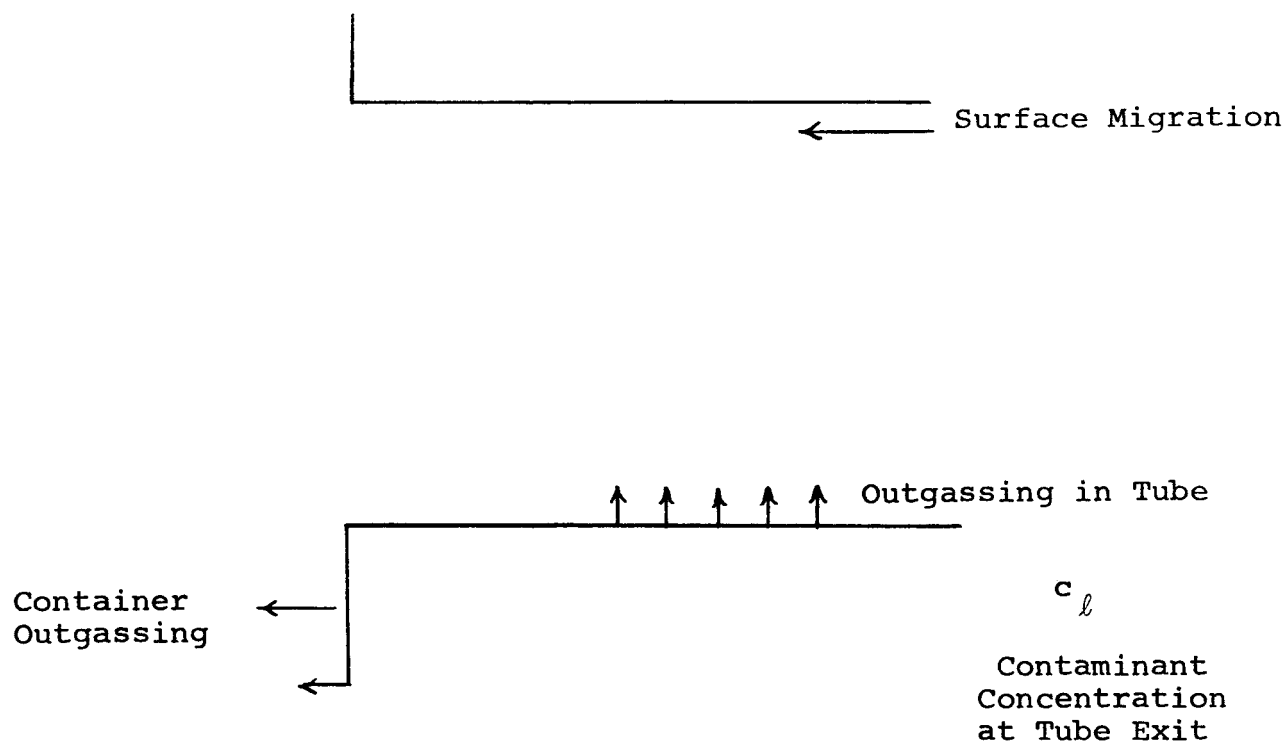
Sources of Contaminant Gases

Figure   1.3

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D

m.f.p. less than $\frac{1}{10}$ D

Viscous

D

m.f.p. greater than D

Molecular
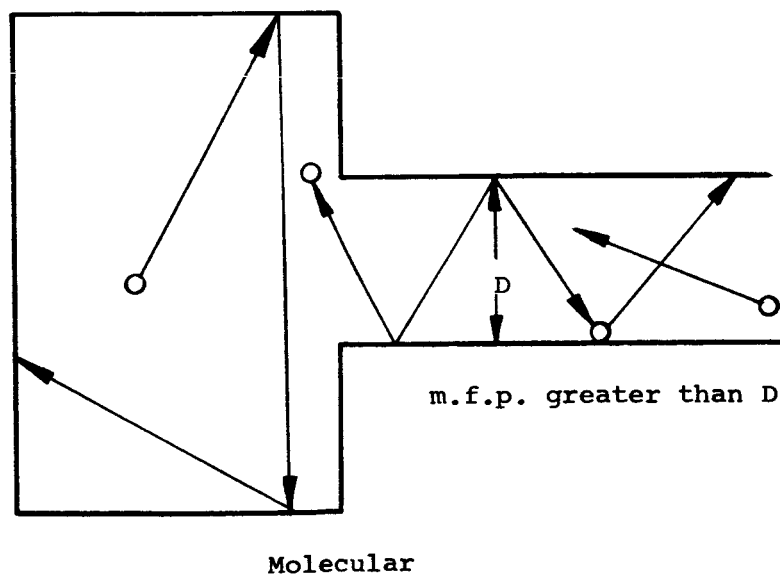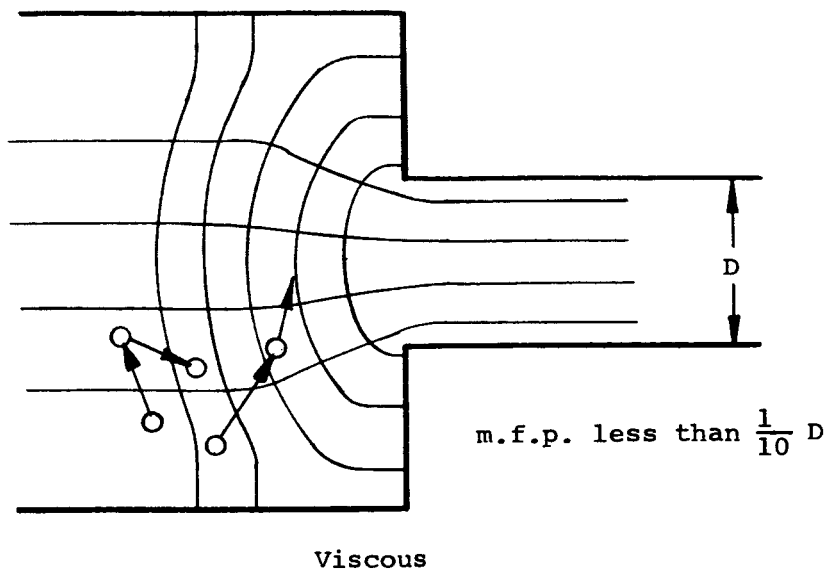
Gas   Flow   Patterns

Fig. 1.4

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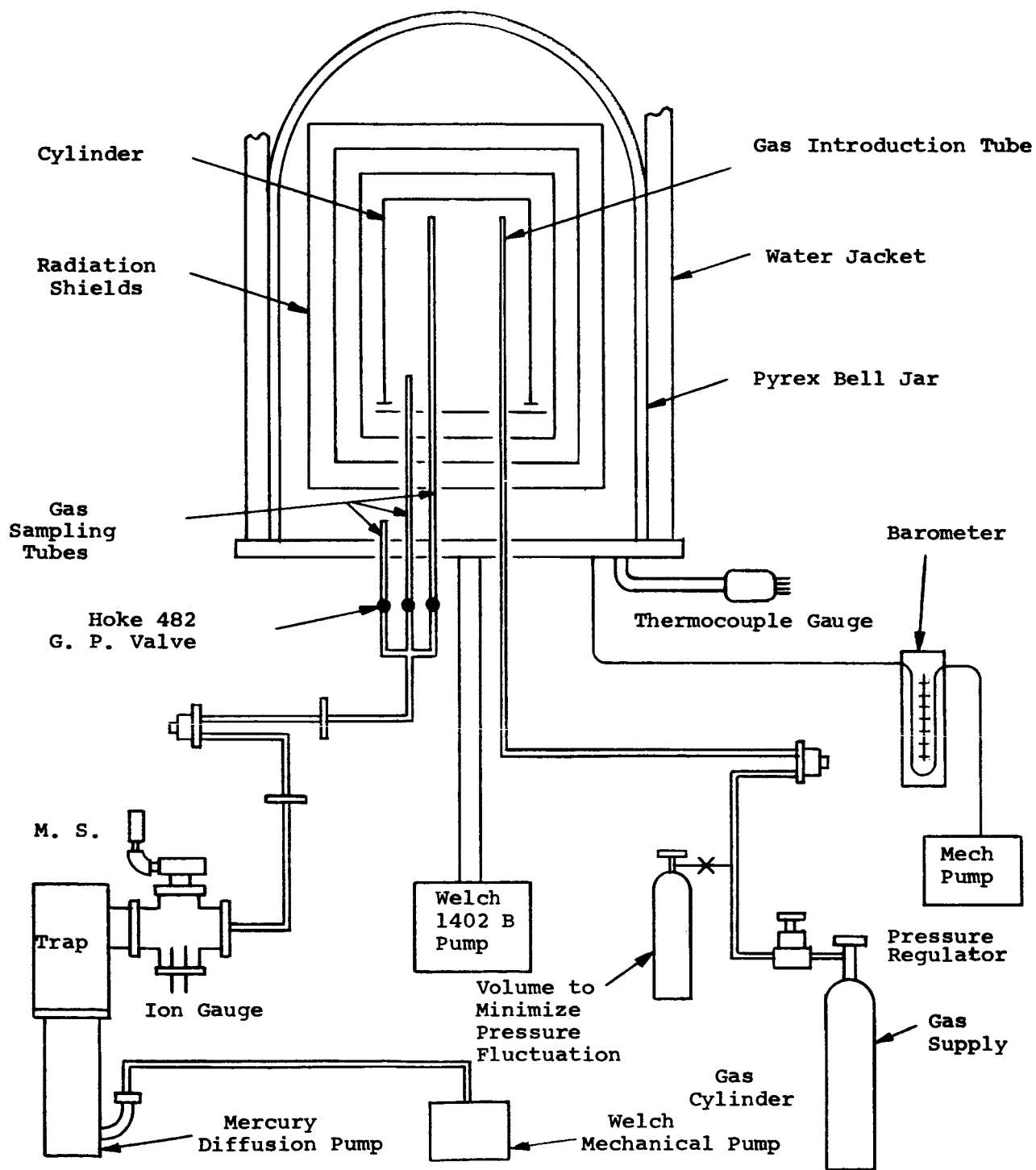
Fig. 1.5

System Schematic

2.0   MATHEMATICAL ANALYSIS

2.0 MATHEMATICAL ANALYSIS

2.1 Upstream Diffusion of a Contaminant Gas in a Pipe Carrying the Inert Gas

One of the possible sources of contamination in a gas bleed system is by upstream diffusion. In order to simplify the analysis of this problem, the following will be assumed:

1. The gas velocity in the pipe is constant, being neither a function of radial or axial position in the pipe.

2. The gas adsorbed on the pipe walls is in equilibrium with the gas concentration at all axial positions in the pipe.

The following nomenclature is used:
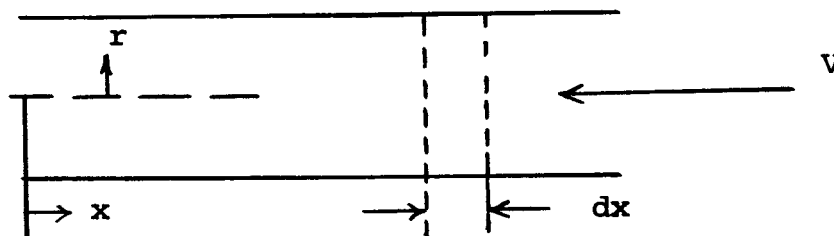
A = cross-sectional area of pipe (cm^2)

D = diffusion coefficient (cm^2/sec)

c = molecular concentration of contaminant molecules (cm^{-3})

V = gas velocity (cm/sec)

Taking an oil mass flow balance in the elemental volume, Adx yields the following:

$$-D\frac{dc}{dx} - Vc - \left[-D \left(\frac{dc}{dx} + \frac{d^2c}{dx^2}\, dx \right) - V \left(c + \frac{dc}{dx}dx \right) \right] = 0 \quad (1)$$

which reduces to

$$\frac{d^2c}{dx^2} + \frac{V}{D}\frac{dc}{dx} = 0$$

and the solution for a pipe of semi-infinite length is:

$$\frac{c}{c_o} = e^{-\frac{V}{D}x} \quad (2)$$

where c_o is the concentration at the pump end. Substituting numerical values into "Equation (2)" yields the following table:

$\dfrac{Vx}{D}$	2.302	4.60	6.91	9.21	11.51	13.82
$\log \dfrac{c}{c_o}$	-1	-2	-3	-4	-5	-6

To obtain an approximate value of the diffusion coefficient, D, the Stefan-Maxwell theory is used, which states (Ref. 2):

$$D_{12} = \frac{(\bar{v}_1^{\,2} + \bar{v}_2^{\,2})^{\frac{1}{2}}}{3\pi \ (c_1 + c_2) \ S_{12}^2} \tag{3}$$

where $\bar{v}$ = average molecular velocity

$S = \frac{1}{2} \ (\sigma_1 + \sigma_2)$

σ = molecular diameter

The diffusion constant in argon (cm/sec) for various gases is listed with the assumed molecular diameter at a temperature of 300°K.

TABLE 2.1

DIFFUSION COEFFICIENTS OF VARIOUS GASES IN ARGON

	Molecular Diameters (10^8) cm.	DP (cm^2/sec) (torr)
H_2O	4.58	124
N_2	3.80	148
O_2	3.62	149
CO_2	4.62	95
Benzene	7.5	46.5
Hg	5.11	67.7
H_2	2.72	535
He	2.20	465
Ar	3.64	

Ref. 2 - Jeans, J., "The Dynamical Theory of Gases."

P_{mm} is the gas pressure in millimeters of mercury. Using "Equations (2) and (4)," a pumping system can be designed that effectively eliminates contamination from upstream diffusion. The following table illustrates the attenuation of mechanical pump oil at several bleed gas pressures in a pipe 2 ft. long and 3/4 in. diameter through which 5 cfm of argon is being pumped.

Argon Pressure P (microns)	Oil Contamination Attenuation $\log c/c_o$
10	-15.1
50	-75.5
100	-151
500	-755
1000	-1510

2.2 Concentration of Contaminant Gases Originating in Test Chamber

2.2.1 In Pump Pipe

One of the predominant contaminants originating in the test chamber is water vapor. At the chamber end of the pump pipe, the contaminant flow is the product of the outgassing rate and the chamber surface area. At the pump end of the pipe, the contaminant partial pressure may be as high as the saturation pressure. Under these conditions the partial pressure of the contaminant in the chamber will be determined when there is a sweeping gas flow in the pipe. As before, the pipe wall contamination will be assumed to be in equilibrium, and the sweeping gas velocity a constant.

Chamber end $\quad \xrightarrow{\quad V \quad} \quad$ Pump end

$x \qquad\qquad x = \ell$
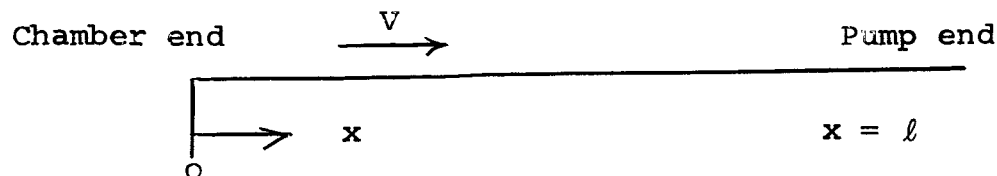
Let c be the molecular concentration of the contaminant and D the diffusivity; then the equation of the flow is:

$$\frac{d^2c}{dx^2} - \frac{V}{D}\frac{dc}{dx} = 0 \tag{5}$$

which has the general solution

$$c = Ae^{\frac{V}{D}x} + B \tag{6}$$

The boundary conditions are:

$$x = 0; \quad q = q_o$$
$$x = \ell; \quad c = c_1$$

where q is the flow rate per unit area of the contaminant and is as follows:

$$q = -D\frac{dc}{dx} + Vc = -AVe^{\frac{V}{D}x} + V\left(Ae^{\frac{V}{D}x} + B\right) \tag{7}$$

therefore $B = \dfrac{q_o}{V}$

and $A = \left(c_1 - \dfrac{q_o}{V}\right) e^{-\frac{V}{D}\ell}$

Substituting these constants into "Equation (6)" and letting $x = 0$, the contaminant concentration at the chamber end of the pipe becomes:

$$c_o = \left(c_1 - \frac{q_o}{V}\right) e^{-\frac{V}{D}\ell} + \frac{q_o}{V} \tag{8}$$

"Equation (8)" was applied to determine the concentration of contaminating water vapor at the furnace end of a 3/4 in. diameter x 2 ft. long pump pipe with 5 cfm flow of argon. The water vapor pressure at the pump was assumed to be the saturation pressure of water at 100°F and the water outgassing rate in the furnace chamber was assumed to be 10^{-7} torr liters/cm^2-sec. The furnace was assumed to contain an argon-swept shroud 3 in. diameter x 6 in. long, and the total outgassing area of the furnace assembly was taken as ten times the surface area of the shroud itself to account for the outgassing of radiation shields, etc. The following water vapor pressures at the pipe inlet were calculated as a function

of argon pressure:

Argon Pressure P (microns)	Water Vapor Pressure P_o (torr)
10	0.76×10^{0}
50	1.74×10^{-3}
100	1.74×10^{-3}
1000	1.74×10^{-3}

It can be seen from this table that between 10 and 50 microns
argon pressure the pump is no longer a significant source of water
contamination, the furnace outgassing being the major contributor.
These pressures were calculated with a diffusion constant that was
determined on the basis of the water molecule concentration being
negligible relative to the argon. This is certainly not true at
the pump end of the pipe if saturation water pressure is assumed;
however, if a correction were made, the diffusivity would be lowered
and the water vapor contamination from the pump would be eliminated
at a lower argon pressure than shown in the table.

2.2.2   In Furnace Shroud

Consider a furnace shroud as shown in the accom-
panying figure with the sweeping gas being introduced at point A
to produce the sweeping velocity, V, and outgassing from the walls
occurring at the rate q_s per unit surface area. What is the con-
taminant concentration as a function of shroud length neglecting
radial variations?
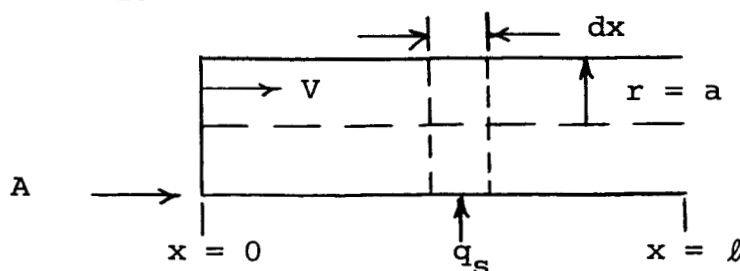
The differential equation of the system is obtained from a

mass balance over the volume element dx.

$$\pi a^2 \left(-D\frac{dc}{dx} + V\right) + 2\pi a \, q_s dx - \pi a^2 \left[-D\left(\frac{dc}{dx} + \frac{d^2c}{dx^2}dx\right) + V\left(c + \frac{dc}{dx}dx\right)\right] = 0$$

(9a)

or

$$\frac{d^2c}{dx^2} - \frac{V}{D}\frac{dc}{dx} = -\frac{2q_s}{aD}$$

(9b)

The solution to "Equation (9b)" is:

$$c = Ae^{\frac{V}{D}x} + \frac{2q_s x}{aV} + B$$

(10)

and the boundary conditions are:

$$x = 0; \quad q = q_s$$

$$x = 1; \quad c = c_1$$

But $\quad q = -D\frac{dc}{dx} + Vc = -D\left(\frac{AV}{D}e^{\frac{Vx}{D}} + \frac{2q_s}{aV}\right) + V\left(Ae^{\frac{Vx}{D}} + \frac{2q_s x}{aV} + B\right)$

so at $x = 0$

$$q_0 = \frac{-2q_s D}{aV} + VB; \quad B = \frac{q_s}{V}\left(1 + \frac{2D}{aV}\right)$$

The constant A is determined from the second boundary condition:

$$c_1 = Ae^{\frac{V\ell}{D}} + \frac{2q_s \ell}{aV} + \frac{q_s}{V}\left(1 + \frac{2D}{aV}\right)$$

$$A = \left[c_1 - \frac{2q_s \ell}{aV} - \frac{q}{V}\left(1 + \frac{2D}{aV}\right)\right] e^{-\frac{V\ell}{D}}$$

and final equation relating contaminant concentration to axial position in the furnace shroud becomes:

$$c = \left[c_1 - \frac{q_s}{V}\left(1 + \frac{2\ell}{a} + \frac{2D}{aV}\right)\right] e^{\frac{V}{D}(x-\ell)} + \frac{2q_s}{aV}x + \frac{q_s}{V}\left(1 + \frac{2D}{aV}\right)$$

(11)

Use of "Equations (3), (8), and (11)" with assumed outgassing rate, q_s, allows the approximate calculation of contaminant concentration in a shroud furnace design.

"Equation (11)" was applied within the furnace shroud of the previous example, and the resulting distribution of contaminating water vapor along the length of the shroud interior is shown in Fig. 2.1 for argon pressures of 500 and 1000 microns.

2.3 Gettering of Contaminant Gases in Test Chamber

A columbium sample heated in an argon-purged tube will have a gettering action for the impurities in the argon stream that will reduce the impurity partial pressure at the sample. This effect will be analyzed on the assumption that the gettering effect of the crucible wall is negligible compared to that of an uncontaminated sample. Consider the following geometry.
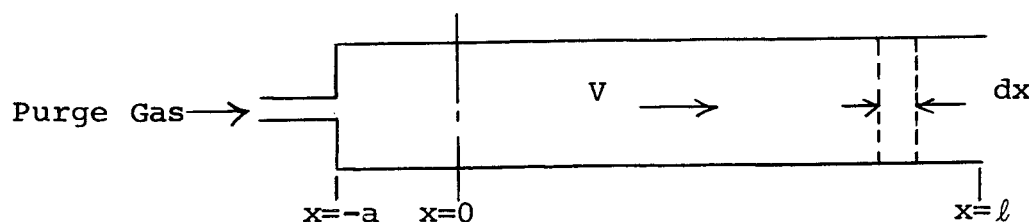
The sample is assumed to be at station x = 0, and its pumping action for impurities will be proportional to the impurity concentration at the sample; flow is assumed to be one dimensional.

$$q_g = kc_o \quad \text{mol./sec. cm}^2 \qquad (1)$$

where q_g = getter pumping flow referred to crucible cross-sectional area (mol./sec. cm^2)

c_o = molecular concentration of impurities at x = 0 (mol./cm^3)

k = proportionality constant depending on sticking coefficient and sample area

At a point in the crucible removed from the sample the impurity flow is described by the equation:

$$q_x = -D \frac{dc}{dx} + Vc \qquad (\text{mol/ sec. cm}^2) \qquad (2)$$

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where   D = diffusion coefficient (cm^2/sec)

V = purge gas mean velocity (cm/sec)

Equation (2) plus the equation of continuity yields the governing differential equation:

$$\frac{d^2c}{dx^2} - \frac{V}{D}\frac{dc}{dx} = 0 \tag{3}$$

This equation has solutions of the form

$$c = C_1 e^{\frac{V}{D}x} + C_2$$

and the boundary conditions are as follows.

$$x = -a$$

$$q = \frac{\rho VN \ (ppm) \ 10^{-6}}{M} \equiv \alpha V \tag{4}$$

where

ρ = sweep gas density (gm/cm^3)

N = Avogadro's number = 6.02×10^{23} (mol/gm-mole)

M = sweep gas molecular weight (gm/gm-mole)

(ppm) = impurity fraction of sweep gas (parts per millicn)

α = impurity concentration in purge gas (mol/cm^3)

At $x = 0$

(a)   The impurity concentration is continuous, therefore:

$$c_o = c_o' \tag{5}$$

where the unprimed quantity refers to the upstream and the primed quantity to the downstream concentrations.

(b)   The net impurity flow must equal the sample gettering rate, therefore

$$q - q' = q_g = kc_o \tag{6}$$

At $x = \ell$

At the crucible exit the impurity concentration is held at

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a prescribed value, c_ℓ.

$$c = c_\ell \tag{7}$$

The solutions for the upstream and downstream portions of the crucible tube are respectively

$$c = Ae^{\frac{V}{D}x} + B$$

$$c' = Ee^{\frac{V}{D}x} + F \tag{8}$$

Equations (4) through (7) allow the evaluation of the constants in equation (8) and the following expression is obtained for the impurity concentration, c_o, at the sample

$$\frac{c_o}{c_\ell} = \frac{\frac{\alpha}{c_\ell}(1 - e^{-\frac{V\ell}{D}}) + e^{-\frac{V\ell}{D}}}{1 + \frac{k}{V}(1 - e^{-\frac{V\ell}{D}})} \tag{9a}$$

or in another form

$$\frac{c_o}{c_\ell} = \frac{(e^{-\frac{V\ell}{D}} - \frac{V}{kc_\ell})}{e^{-\frac{V\ell}{D}} - 1 - \frac{V}{k}}(1 - e^{-\frac{V\ell}{D}}) + e^{-\frac{V\ell}{D}} \tag{9b}$$

Several useful limiting cases can be obtained from equation (9).

Zero gettering action (k = 0)

$$c_o/c_\ell = \frac{\alpha}{c_\ell}(1 - e^{-\frac{V\ell}{D}}) + e^{-\frac{V\ell}{D}} \tag{10}$$

Zero purge gas impurity ($\alpha = 0$)

$$c_o/c_\ell = \frac{e^{-\frac{V\ell}{D}}}{1 + \frac{k}{V}(1 - e^{-\frac{V\ell}{D}})} \tag{11}$$

Zero sweeping velocity $(V = 0)$

$$c_o/c_\ell = \frac{1}{1 + \frac{k\ell}{D}} \qquad (12)$$

Infinite sweeping velocity $(V \rightarrow \infty)$

$$c_o/c_\ell = \frac{\alpha}{c_\ell} \qquad (13)$$

Although the gettering factor, k, is in a useful form for the foregoing derivation, a different form is more useful for purposes of computation. From kinetic theory, the rate at which gas molecules strike a surface is:

$$\frac{1}{A}\frac{dn}{dt} = \frac{1}{4}\bar{v}\,c \quad \text{mol/cm}^2\text{sec}$$

where $\bar{v}$ = average molecular velocity

If s is the fraction that stick upon striking the surface, then

$$k = \frac{s\bar{v}}{4}\left(\frac{S_s}{S_T}\right) = \frac{s}{4}\left(\frac{S_s}{S_T}\right)\sqrt{\frac{8R_oT}{\pi M_c}} \qquad (14a)$$

where S_s/S_T = ratio of sample surface area to crucible tube cross-section

M_c = molecular weight of contaminant (gm/gm-mole)

R_o = gas constant = 8.32×10^7 erg/^{o}K gm-mole

T = gas temperature (^{o}K)

Evaluating equation (14a) yields

$$k = 3.64 \times 10^3\, s\, \left(\frac{S_s}{S_T}\right)\sqrt{\frac{T}{M_c}} \qquad \text{(cm/sec)} \qquad (14b)$$

For ease in calculation, the impurity concentration, α, is best manipulated into the following form by use of the ideal gas law.

$$\alpha = 0.963 \times 10^{13}\,\frac{p\ (\text{ppm})}{T} \quad (\text{mol/cm}^3) \qquad (15)$$

where p = purge gas pressure (torr)

Likewise, the impurity concentration at the crucible mouth, c_ℓ, can be put in terms of pressure and temperature,

$$c_\ell = 0.963 \times 10^{19} \frac{p_c}{T} \qquad (\text{mol/cm}^3) \qquad (16)$$

where p_c = contaminant gas partial pressure surrounding crucible (torr)

The diffusivity coefficient, D, is functionally related to temperature as follows

$$\frac{D_1}{D_2} = (\frac{T_1}{T_2})^{3/2} \qquad (17)$$

For the particular case of diffusion of oxygen or nitrogen in argon, the relationship becomes,

$$D = \frac{D_o}{p} (\frac{T}{300})^{3/2} \qquad (\text{cm}^2/\text{sec}) \qquad (18)$$

where $D_o \approx 149$

Equation (9) was used to compute the contaminant concentration in the experimental crucible tube at 2000°F with the slight modification that c_o/c_ℓ' is plotted, where c_ℓ' is the contaminant concentration at the pumping port which is at room temperature. The relationship between the two ratios is simply

$$c_o/c_\ell' = (\frac{T_{room}}{T_{crucible}}) \ c_o/c_\ell$$

The results are shown in Fig. 2.2 with the sticking coefficient being chosen at s = 0, (no gettering action), and s =0.1 (perfect gettering action.) The upper curve (s = 0) can be seen to be a smooth transition between two straight lines on a semilog plot; the straight diagonal line ($c_o/c_\ell = e^{-V\ell/D}$) being the exit impurity attenuation for a perfectly pure purge gas, and the horizontal line ($c_o/c_\ell = \alpha/c_\ell$ being the ratio of purge gas initial

impurity to the impurity of the atmosphere at the crucible exit.
At the higher values of sticking factor, s, the purity level at
the sample, c_o, is improved due to the pumping action of the sample,
but as the purge gas velocity is increased, the improvement dimin-
ishes due to the greater absolute amount of impurity introduced
by the purge gas. At infinite velocity all curves approach the
value $(c_o/c_\ell = \alpha/c_\ell)$ irrespective of sticking factor.

Although a non-zero sticking factor increases the purity of
the shielding atmosphere at the specimen, the conservative approach
is to design a system assuming that s = 0, and to consider the
gettering action as a bonus. This design philosophy will be followed
in this report.

In a purged system of the type under consideration, with a
given gas purity and geometry, the impurity concentration at the
specimen can be reduced continuously by decreasing the purge gas
pressure and increasing the velocity (larger pump). Theoretical
limitations exist, however, for two reasons: (1) when pressure is
reduced to the point where continuum flow ceases to exist, the
developed equations break down; (2) practically speaking, the gas
velocity is limited to a subsonic value. The first limitation can
be established by considering the ratio of the crucible tube dia-
meter to the mean free path of the purge gas molecules, the Knudsen
number $(N_k = \lambda/d)$. The theoretically developed equations hold with
reasonable accuracy down to a value of $N_k = 10$. For argon at 25^oC
and at a pressure of 1 torr the mean free path is approximately
.0053 cm, (Ref. 1) and as is approximately a function of density
only, the mean free path can be expressed as:

$$\lambda_{argon} \doteq 5.3 \frac{T}{298} \frac{10^{-3}}{p} = 1.78 \times 10^{-5} \frac{T}{p} \quad (cm). \quad (19)$$

From the practical standpoint, the purge gas velocity will be
limited by the pump size for economic reasons. If a system of fixed
geometry and purge gas purity (ppm) is considered, a required value
of impurity concentration, c_o, can be obtained with a range of

Ref. 1. Dushman. 2nd edition. pg. 32.

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pump size and pressure levels. This can be seen from Fig. 2.3 which represents such a system. With a constant value of c_ℓ, a horizontal line is a constant value of c_o; the various curves represent several system pressure levels. It can be seen that there exists a pressure curve that intersects the required value of c_o at a lower velocity (or pump size) than any other pressure. The dashed envelope on Fig. 2 represents this condition, and the equation for this locus of optimum pressure will be found

Equation (10) is re-written, assuming that $(e^{-\frac{V\ell}{D}}) \ll 1$.

$$c_o/c_\ell = \frac{\alpha}{c_\ell} + e^{-\frac{V\ell}{D}} \tag{20}$$

or

$$c_o/c_\ell = K_1 p + e^{-K_2 V p}$$

where

$$K_1 = \frac{\alpha}{c_\ell p} = \frac{0.963 \times 10^{13} \text{ (ppm)}}{c_\ell T}$$

$$K_2 = \frac{\ell}{D p} = \frac{\ell}{D_o (\frac{T}{300})^{3/2}}$$

To find the optimum value of p for which V is a minimum at a given c_o and $\frac{\alpha}{c_\ell}$, $(\frac{\partial V}{\partial p})$ is equated to zero.

$$(\frac{\partial V}{\partial p}) /c_\ell = \frac{K_1}{K_2 p (c_o/c_\ell - K_1 p)} + \frac{\ln_\epsilon (\frac{c_o}{c_\ell} - K_1 p)}{K_2 p^2} = 0$$

$$\therefore \quad \ln_\epsilon (\frac{c_o}{c_\ell} - K_1 \hat{p}) = 1 - \frac{c_o/c_\ell}{(\frac{c_o}{c_\ell} - K_1 \hat{p})} \tag{21}$$

Unfortunately, equation (21) can not be explicitly solved for optimum pressure, $\hat{p}$; however, the equation has been plotted in Fig. 2.4 and this curve can be used to determine $\hat{p}$ after K_1 and c_o/c_ℓ have been calculated. Equation (21) has two solutions for $\hat{p}$, and if

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Figure (3) need be extended in range it must be borne in mind that a negative solution of $\hat{p}$ exists which must be discarded. The minimum velocity is then obtained from Equation (20).

$$V_{min} = \frac{- \ln_\epsilon \left(\frac{c_o}{c_\ell} - K_1 \, \hat{p} \right)}{K_2 \, \hat{p}} \qquad \text{(cm/sec)} \qquad (22)$$

The necessary equations are now at hand to set up a calculation scheme to determine the best pumping speed and pressure to obtain the required c_o in a given system.

Known quantities (c.g.s.)

1. system geometry
2. crucible temperature, T
3. outgassing rate of system enclosure, $\dot{q}$ $\left(\frac{torr \ liters}{cm^2 \ sec} \right)$
4. purity of purge gas, (ppm)
5. required impurity concentration, c_o

Computation procedure

1. Estimate impurity concentration at crucible opening, c_ℓ
2. From Equation (21) calculate p (use Fig. 3)
3. From Equation (22), calculate V
4. Calculate speed of the pumping system
   $$\dot{Q} = VS_T \left(\frac{T_{ambient}}{T} \right) 10^{-3} \qquad \text{(liters/sec)}$$
5. Calculate c_ℓ
   $$c_\ell = 3.53 \ (10^{16}) \ \frac{\dot{q} \ (A_{enclosure})}{\dot{Q}} \left(\frac{T_{ambient}}{T} \right) \qquad (mol./cm^3)$$

   and return to step (2).

2.4 Surface Migration

Passage of oil into the chamber by surface migration from the oil-sealed mechanical pump along the walls of the interconnecting lines to the work space is another contamination source.

In order to discuss surface migration, it is necessary to consider

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·the interaction of a surface and a gas molecule. First, if we take
two particles and move them closer together, the interaction force
is shown on Fig. 2.5. E is the energy required for the molecules to
separate an infinite distance. Now, if we assume a solid surface
appears to another molecule as shown on Fig. 2.6, then the energy
required for a molecule to hop between any two adjacent surface
molecules is less than the energy for the molecule to escape from the
surface. The energy associated with escape from the surface or
evaporation is known as the heat of vaporization. It can be seen that
as a molecule hops across a surface, there is a transfer from the
gas phase to the solid surface as well as along the surface. The rate
at which the molecules move is related to the distance for each hop
and the frequency of the hop. DeBoer shows that the frequency of hops
is related to the basic lattice vibrational frequency and the activa-
tion energy.

$$D_s = K\ell\tau_o e^{-U_s/RT}$$

E_s = energy required for adsorbed molecule to hop
      along surface

ℓ = distance of hops

K = characteristic constant of equation

D_s = surface diffusion coefficient

τ_o = vibrational frequency of lattice

R = gas constant

T = temperature of molecules

The rate at which molecules are transferred is:

$$q_s = D_s a \frac{d\sigma}{dx}$$

$\frac{d\sigma}{dx}$ = concentration difference per unit distance
       mole/cm^2/cm

a = area for transport

q_s = molecules transported per second

Examination of this equation reveals that as the temperature is
raised, the number of molecules transported increases. However, we

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have a competing process. Evaporation of the molecules is also
taking place and can be shown to be:

$$\eta_e = \sigma/\tau$$

σ = number of molecules on surface

τ = residence time on surface and $\tau = \tau_o e^{E/RT}$

η_e = evaporation rate

E = activation energy for evaporation

Therefore, the number of molecules existing on the surface decreases
with increasing temperature. Surface migration can be stopped by
either of two techniques, one by cooling the surface so that the
molecules do not move freely and the other by essentially boiling
them off.

Fig. 2.7 shows the relationship of the surface concentration,
diffusion constant, and migration rate as a function of reciprocal
temperature. Note that surface concentration increases as temperature
decreases. Also, the surface concentration has a stronger dependence
on temperature than the diffusion constant. This means the migration
rate which is the product of and D_s is continually increasing as
temperature decreases.

Both processes were put in a single expression and the
results are displayed in Figs. 2.8 and 2.9. The particular situation
described is for migration along a uniform metal surface with evapora-
tion taking place. It was also assumed that the space above the
surface was maintained at zero pressure.

The figures show the molecular transfer rate for a parti-
cular surface migration activation energy and evaporation energy as a
function of temperature. The distance of a hop was taken to be that
of the molecular spacing of a metal, 3×10^{-8} cm. A minimum residence
time of 3×10^{-14} sec. corresponds to the vibrational frequency of
a lattice at normal temperatures. The surface concentration of oil
molecules at the start of the metal surface was taken to be 10^{15}
molecules/cm^2.

2.5 Pressure Variation Due to Sinusoidal Gas Flow Through the Pump

The gas bleed pressure is usually maintained by having a constant rate of in leakage, q_o, into a volume and removing this gas with a positive displacement pump. The pump is generally an oil-sealed piston or rotary vane type. Both types of these pumps do not have a constant pumping speed as a function of time. Rather, their instantaneous speed probably varies sinusoidally. Assume S = average pumping speed of pump

$$S = (1 + \sin wt) = \text{instantaneous pumping speed}$$

where   w = angular velocity of pump

         t = instantaneous time

         V = volume of chamber associated with q_o and S

The differential equation describing the speed is:

$$V\frac{dp}{dt} + pS (1 + \sin wt) = q_o$$

The solution to the above equation is:

$$p - p_{avg} = \frac{q_o}{S} \left[(\exp \frac{S}{Vw} \cos wt) -1 \right]$$

Typical mechanical pumps have angular velocities of approx. 50 rad./sec (Welch 1402, 5 ft^3/min pump).

See Fig. 2.10 for maximum pressure variations for various S/V ratios.

The sinusoidal pumping speed may also cause back diffusion of gases up the interconnecting tubes during the period of low or zero pumping speed.

This does not appear to be a problem except for very small volumes or high pumping speeds.

2.6 Resonant Frequency of Cavity

A further problem that may be associated with the sinusoidal pumping speed is the chamber volume may have a resonant frequency approaching the pump frequency. Again this was found not to be a problem in normal pumping systems. The resonant frequency was taken

$$v = \frac{1}{2\pi} c \sqrt{\frac{c_o}{V}}$$

c = velocity of sound = 34,400 cm/sec

V = volume of resonator

c_o= length of tube or in case of orifice, the diameter of the orifice

v = resonant frequency in cycles/sec.

for a c_o = 75 cm.

$$V = 30,000 \text{ cm}^3$$

$$v = \frac{1}{2\pi} (34,400 \text{ cm/sec} \sqrt{\frac{75 \text{ cm}}{30,000 \text{ cm}^3}} = 274 \text{ cycles/sec.}$$

The pump frequency is far below this at approx. 8 cycles/sec.

2.7 Partial Pressure of Impurities in Test Volume

Based on the previous analysis of contaminant backstreaming a simplifying assumption can be made. In a particular volume where the length is approximately equal to the diameter, concentration can be assumed to be uniform and equal to the impurity leak rate divided by the net pump speed.

Proper design of the furnace purge gas system would reduce all outgassing effects from other parts of the chamber.

WATER CONTAMINATION

IN FURNACE SHROUD

Shroud Size: 3 in. dia. x 6 in. lg.

Furnace Area: 10 x Shroud Surface Area

Argon Flow: 5 cfm

Outgassing Rate: 10^{-7} t-ℓ/sec-cm^2
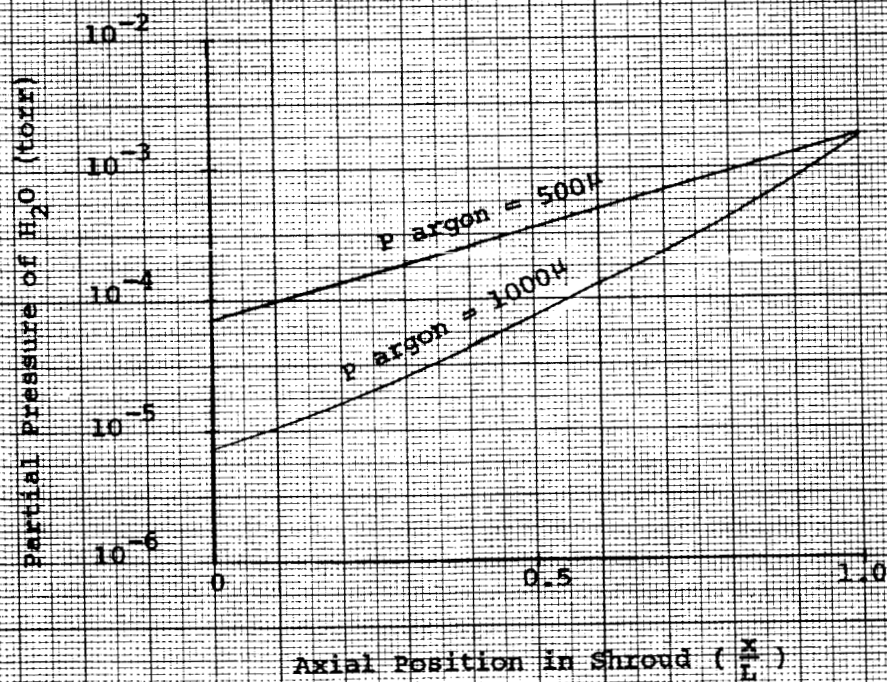
Pipe Size: 0.75 in. dia.x 2 ft. lg.

Partial Pressure of H_2O (torr)

10^{-2}

10^{-3}

10^{-4}

10^{-5}

10^{-6}

P argon = 500μ

P argon = 1000μ

0   0.5   1.0

Axial Position in Shroud ($\frac{x}{L}$)

Figure 2.1

Impurity Attenuation as a
Function of Pump Capacity

System Parameters
    Tube ID = .94"
    Tube length = 5'

Figure 2.2

System Parameters
    Impurity concentration of
    purge gas = 10 ppm
    Temp. of tube = 2000°F
    Exit impurity concentration=
    7.06 x 10^13 mol/cm^3
    (Equivalent to a partial
    pressure of nitrogen of
    10^-2 torr at pumping
    system inlet)
    Purge gas pressure = .25 torr

$\frac{c_o}{c_\ell}$

s = 0

s = .1

(cfm)

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Impurity Attenuation as a
Function of Pressure

Zero Gettering Action

Figure 2.3

Gas Pressure

P_1
P_2
P_3
P_4

Attenuation Ratio (c_o / c_ℓ)

Gas Velocity (V)

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Eq. (21) $\ln_\epsilon (\frac{c_o}{c_\ell} - K_1\hat{p}) = 1 - \dfrac{c_o/c_\ell}{(\frac{c_o}{c_\ell} - K_1\hat{p})}$

Figure 2.4

Plot of Dimensionless Parameter for Determining Optimum Pressure

c_o/c_ℓ

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Repulsive

Distance of Separation

Interaction Energy

Attractive

FORCES BETWEEN TWO MOLECULES

Figure 2.5

Repulsive

Distance of Separation

Interaction Energy

Attractive
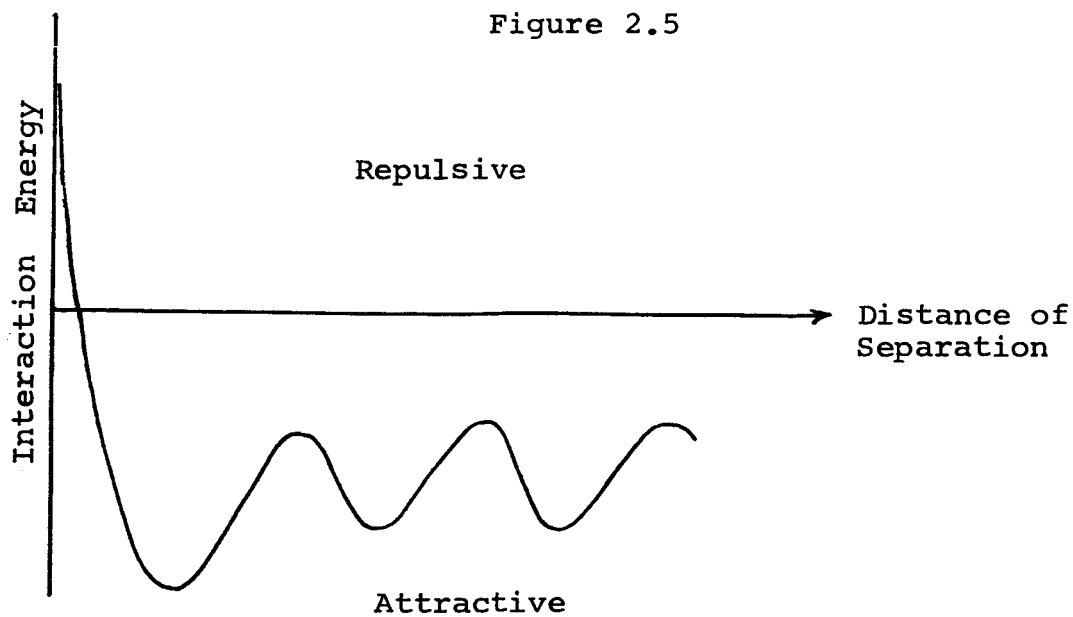
Forces Between Molecules on a Surface

Figure 2.6

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MIGRATION RATE AS A FUNCTION OF TEMPERATURE

Migration
Rate

Surface
Concentration

Surface
Migration
Rate

Slope =
(m−a) < m

Slope = a < m

Slope = m

Diffusion
Constant

$(TEMPERATURE)^{-1}$

Figure 2.7

MIGRATION RATE FOR ZERO SURFACE MIGRATION
ACTIVATION ENERGY AS A FUNCTION OF TEMP.

10^{-6}

10^{-8}

10^{-10}

80
Kcal

40
Kcal

10^{-12}

20
Kcal

10
Kcal $= U_e$

10^{-14}

Migration Rate
t–ℓ/sec–cm.

$L = 10$ cm

$U_s = 0$

10^{-16}

10^{-18}

Molecules Evaporated–
Removed Permanently

10^{-20}

$\sigma_1 = 10^{15} \dfrac{\text{mole}}{\text{cm}^2}$

$\sigma_o = 0$

10^{-22}

Slab at T°K

Min. Time Lag 128 Sec L^2
(L in cm). (For equilibrium
to be established).

10^{-24}

Figure 2.8

0   1   2   3   4   5   6   7   8   9

$1/T \times 10^3$ °K

34

10^{-6}

10^{-8}

$U_s = 0$

10^{-10}

10^{-12}

$U_s = 5$ cal/mole

10^{-14}

10^{-16}

Migration Rate

10^{-18}

Migration Rate as a Function

t-ℓ/sec-cm

of Temp. for Heat of Vaporization =

$20 \dfrac{Kcal}{mole}$

10^{-20}

10^{-22}

10^{-24}

10^{-26}

$U_s = 10$ Kcal/mole

10^{-28}

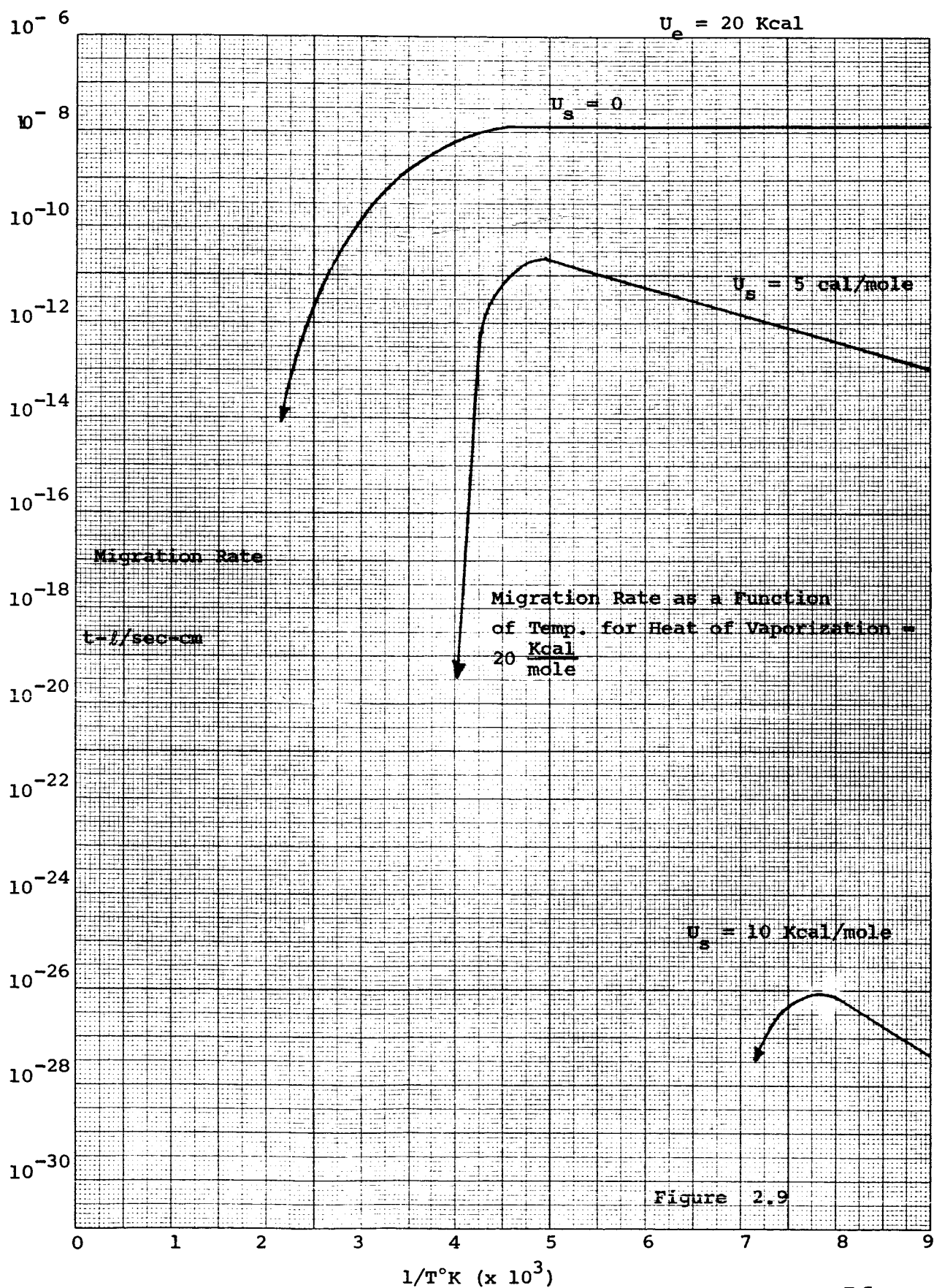10^{-30}

Figure 2.9

0   1   2   3   4   5   6   7   8   9

$1/T°K$ (x 10^3)

PERCENT PRESSURE VARIATION FOR VOLUME, V, SINUSOIDAL PUMPING SPEED S (AVG. SPEED) AND ANGULAR VELOCITY w = 50 RAD.?SEC.

$S = (1 + \sin wt)$

Percent Pressure Variation

s/V (SEC^{-1})

Figure 2.10

3.0 IMPURITY ANALYSIS

3.0 IMPURITY ANALYSIS

At present the experimental phase is using a mass spectrometer and special valving to monitor purity of the incoming gas. The arrangement is shown schematically on Fig. 3.1. Background pressures are routinely attained in the low 10^{-9} torr range and are reasonably stable so that 10% changes in the carbon monoxide, water and hydrogen peaks can be seen while other gases can be seen at higher sensitivities. The maximum total pressure the spectrometer can be used at is 5×10^{-5} torr. Based on the above experimental results, 10 ppm of water, carbon monoxide, and hydrogen can be detected while approximately 1 ppm can be seen of other gases.

While the spectrometer has given satisfactory results, it is necessary that tne purity of the gas, as well as partial pressure detectability be increased in order to extend the applicability of the process.

Mass Spectrometer

The mass spectrometer is capable of detecting approximately 1 - 10 parts per million of impurity in the bleed gas. This was attainable after considerable effort. The additional effort had to be expended in order to achieve these sensitivities on a more routine basis. Following are the results of the study which made this possible. Two areas were investigated; higher magnetic field in the deflection spectrometer, and lower ionizing potential.

Higher Magnetic Fields

The spectra taken with the 3 kilogauss magnet indicated a blending together of the peaks. This was particularly troublesome since the peaks 40 and 28 could not be resolved to base line when the 40 peak was approximately 3×10^{-6} amps and the 28 peak was 3×10^{-10} amps. Typical spectrum is shown in Fig. 3.2. Because of this, it became necessary to improve resolution in some manner. The first technique considered was the use of a higher magnetic field in the mass spectrometer. This should increase resolution since the mass peaks

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occur at greater voltage separation than with the lower field
magnet. A 5.1 kilogauss magnet was installed, and the resolution
indicated a marked improvement. See Fig. 3.3. The desired resol-
ution was attained, and the detectable mass range was extended to a
molecular weight of 200. See Fig. 3.4.

Electron Ionizing Potential

Raising the pressure resulted in peaks which did not appear to
originate in the incoming gas, but were related to the number of ions
formed in the system. The diagnosis was that the ions formed were
desorbing surface gases from the walls. This was not definitely
proven; however, the spurious signals were removed by turning off
the ion gauge and operating the mass spectrometer at a low ionizing
potential (30 v) and a low emission current (.5 ma).

Linearity and Stability of Mass Spectrometer

The linearity and stability of the mass spectrometer was
checked over a period of time and range of pressures. The results
are indicated in Fig. 3.5. The graph indicates a linear relation-
ship between a calibrated ion gauge and the mass spectrometer.

Calibration of High Pressure Gauges

Data by Westinghouse for their Schulz-Phelps gauge indicated
good linearity of the output for pressures of nitrogen up to .5
torr and a saturation limit of 2.5 to 16 torr. Our data did not indi-
cate this to be the case for argon. Linearity could not be ob-
tained up to a pressure of .100 torr. For this reason and since great
accuracy in measurement of pressure is not required for this experi-
ment, a thermocouple gauge was used.

Technique

The thermocouple gauge was calibrated against a pressure
obtained by bleeding gas at a measured rate into a vessel being
pumped at a known speed. The bleed rate was measured volumetrically
at atmospheric pressure in a water-sealed burette. The pumping speed
was obtained with a critical flow orifice having a diameter of 1/16
inch. The calculated speed of the orifice is shown on Fig. 3.6 and

the calibration curve is shown in Fig. 3.7.

Experimental Verification of Analysis

In the experiment nitrogen was used as the contaminant since its concentration can be more readily measured than oil or water. Nitrogen has a short residence time and is relatively inert (especially when a thoriated iridium mass spectrometer filament is used). Less than ten ppm of nitrogen impurity could be routinely measured.

Experimental Apparatus

The experimental apparatus is sketched in Fig. 3.8. A 28 liter bell jar mounted on a plate provided the main chamber working volume. The experimental crucible was mounted within the bell jar. The crucibles were 3", 2-1/2" and 1" in diameter. All were 7" long. This container simulated a high temperature zone for heating the samples. Hi purity argon enters near the closed end of the crucible and flows outward to the pump line. Three 1/8" D probes are provided to sample the gas at various locations. Two probes were located within the crucible and the third outside the can 2-3/4" from the crucible's lower edge. Two separate oil sealed mechanical pumping systems were used. One system provided a pumping speed of 2 liters/sec $\pm$ 10%. The other system provided a pumping speed of 5.4 liters/sec $\pm$ 10%.

In addition to the above, a controlled impurity gas system was needed. Nitrogen, the chosen impurity, was introduced into the bell jar through a probe located approximately 3-1/2 inches above the top of the crucible.

Results

The experiments performed with the various size crucibles and pump speeds resulted in the data plotted in Fig. 3.9. This data indicates the benefit of the purge action of the gas. The data is plotted with c/c_o as the ordinate and $\dot{q}x/D^2$ as the abscissa. C represents the impurity concentration at a distance x from the end of

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the crucible. The diameter, D, of the crucible, the amount of purge gas flowing, $\dot{q}$, and the impurity concentration at the exit c_o, are independent variables. The diffusion coefficient of N_2 in argon was assumed to be $148/P$ (cm^2/sec) for P in torr. The results are plotted under the assumption that the incoming gas had "0" impurity concentration.

A standard procedure for determining the c/c_o ratio was as follows:

1. Shut off purge gas. Obtain base pressure with mechanical pump operating.

2. Nitrogen flow was adjusted with a needle valve until the total pressure, as determined with an oil manometer, was measured as 1 torr.

3. The nitrogen was then shut off with an on-off valve leaving the needle valve at the same setting.

4. The purge gas (argon) was then adjusted a predetermined value.

5. The nitrogen on-off valve was opened. The total pressure was measured and found to be the sum of the argon and nitrogen partial pressures.

6. The mass spectrometer was used to determine the relative proportion of nitrogen to argon within the crucible and outside the crucible.

The nitrogen pressures were varied from .05 torr to 10 torr with the data points falling as shown on the attached Fig. 3.9.

Early in the experimental phase there was considerably more scatter in the data than is now present. This was traced to a faulty pressure regulator on the purge gas line. The regulator was changed and a ballast volume (approximately 2 ft^3) added to maintain the pressure constant. The data was much more consistent after taking this action.

Mass Spectrometer

Pressure Regulator

LN$_2$ Trap

G. P. Valve

Gas Supply Tank

To Vacuum Pumping System
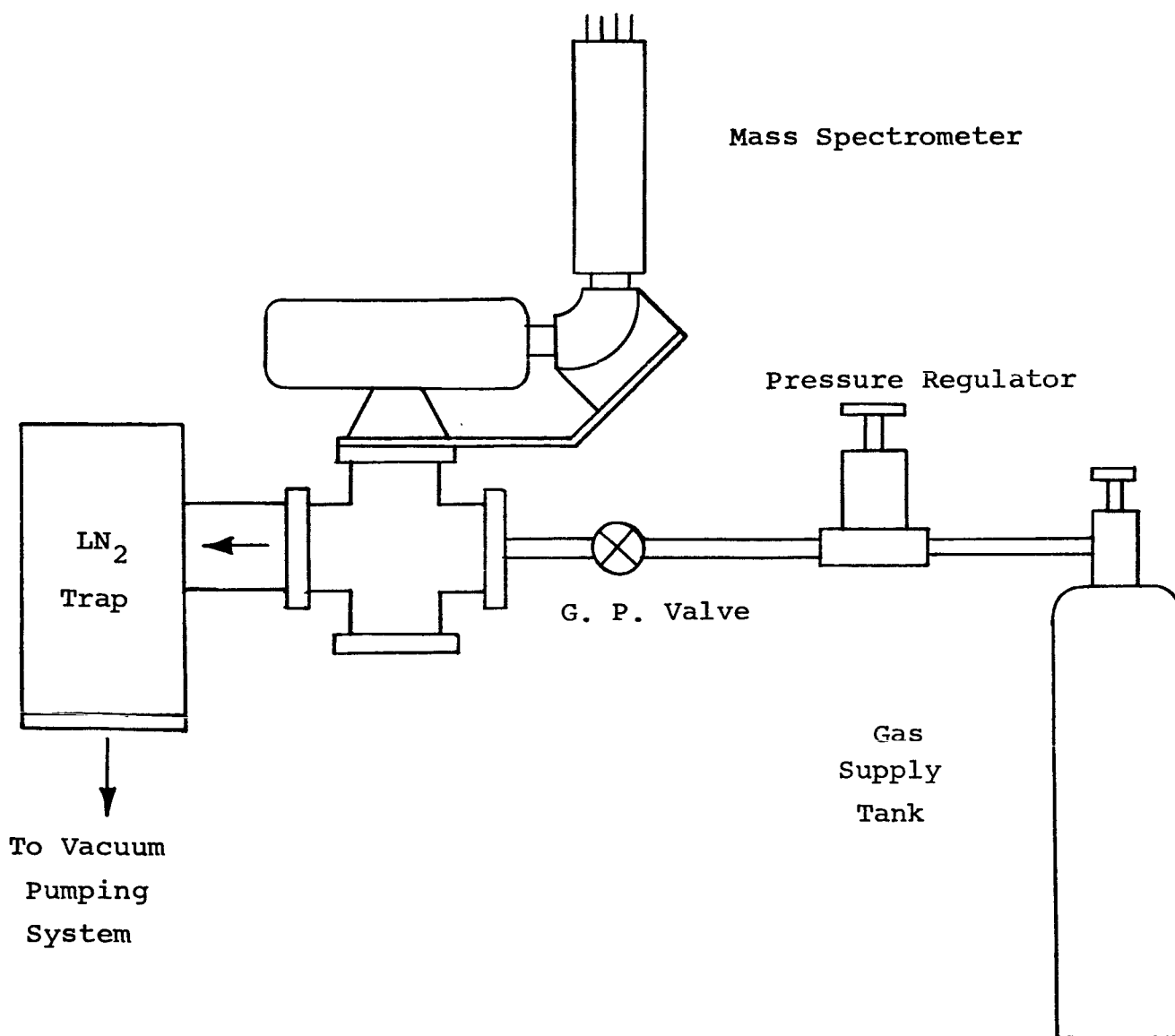
SCHEMATIC OF EXPERIMENTAL SETUP

FOR MONITORING GAS PURITY
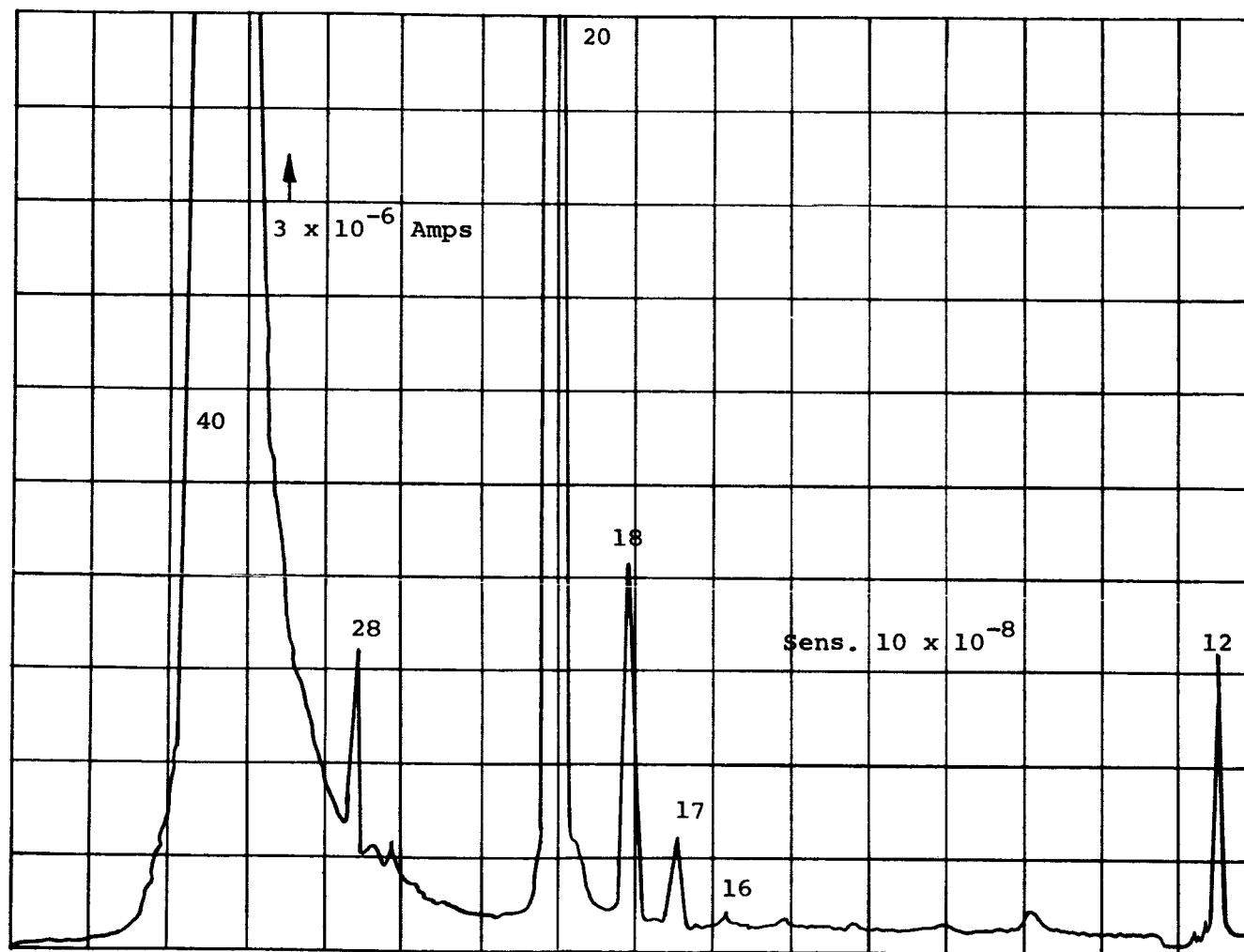
Figure 3.1

Date: 8/26/63

Pressure: 5.3×10^{-5}

Sensitivity: 3×10^{-9} Amps Full Scale

Magnet: 3 Kg

Ionizing Voltage: 50 V

Spectrum Demonstrating Resolution with a 3×10^{-6} Amps

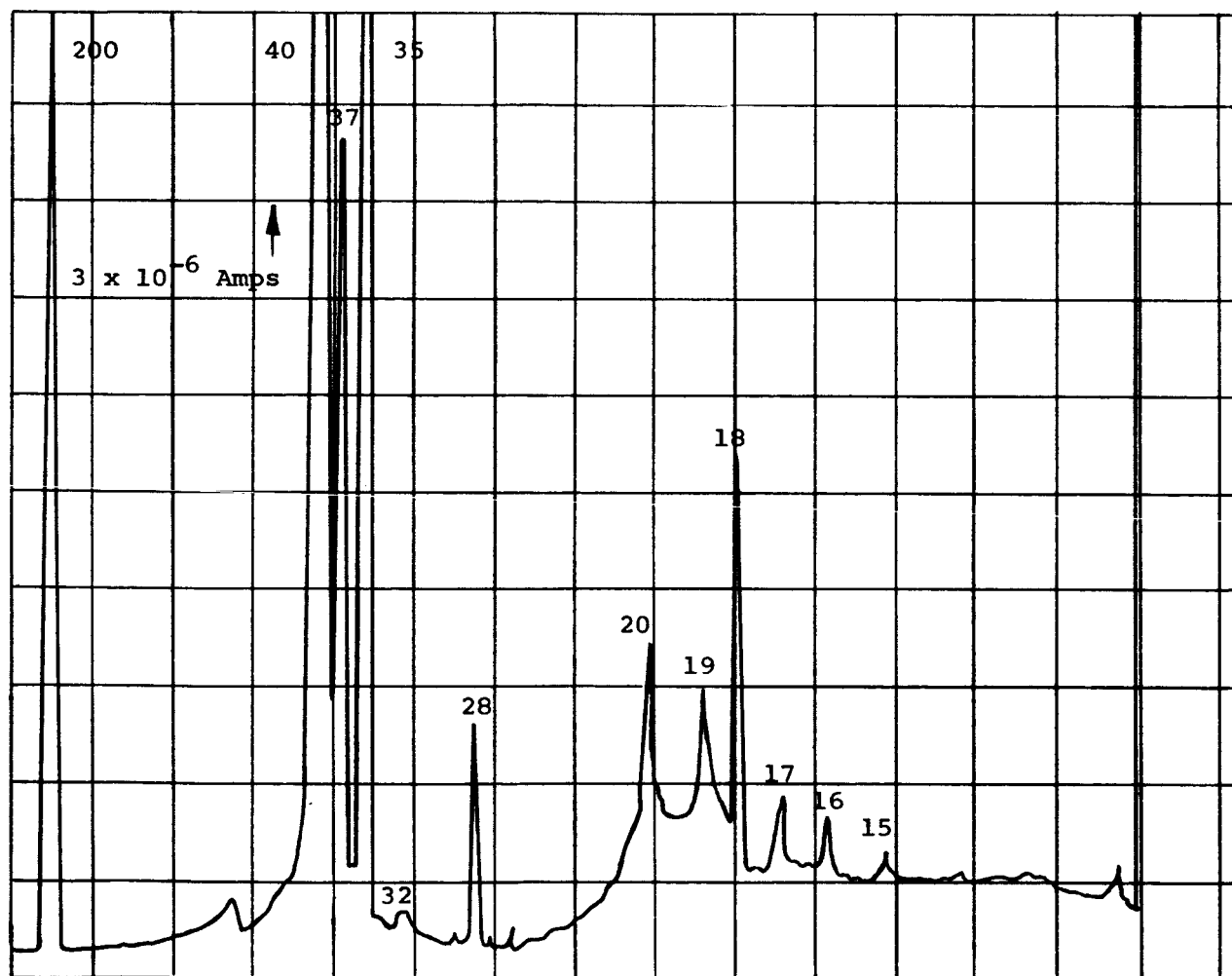Argon 40 Peak with a Full Scale Sensitivity of 3×10^{-9} Amps

Fig. 3.2

Date: 11/5/63

Pressure: 6.8×10^{-6}

Sensitivity: 3×10^{-9} Amps

Ionizing Potential: 30 V

Magnet: 5.1 Kg

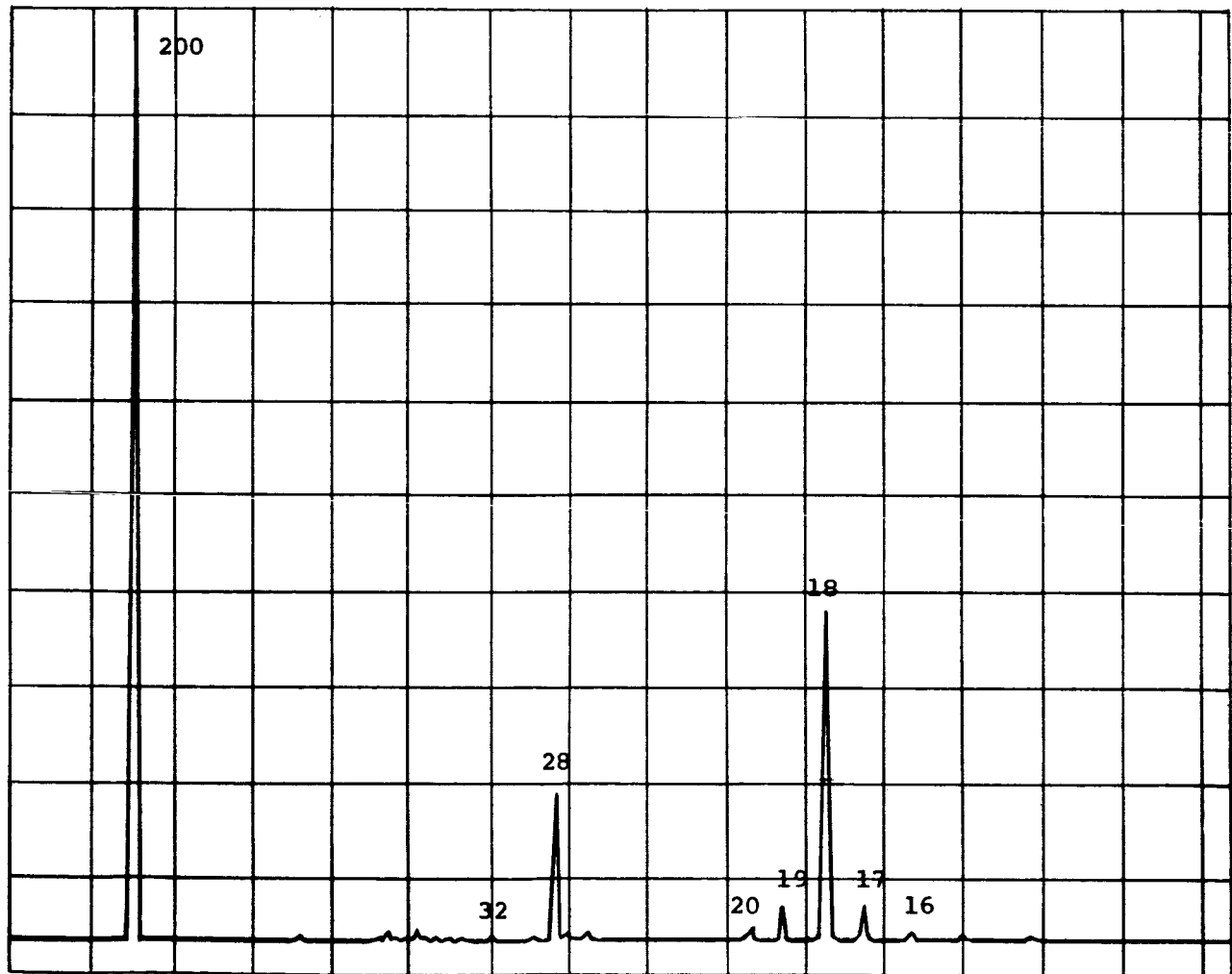Spectrum Demonstrating Increased Resolution with 5.1 Kg

Fig. 3.3

Date: 11/5/63

Pressure: 5.5×10^{-8}

Sensitivity: 3×10^{-9} Amps Full Scale

Magnet: 5.1 Kg

Ionizing Potential: 30 V

Mercury Contaminated System
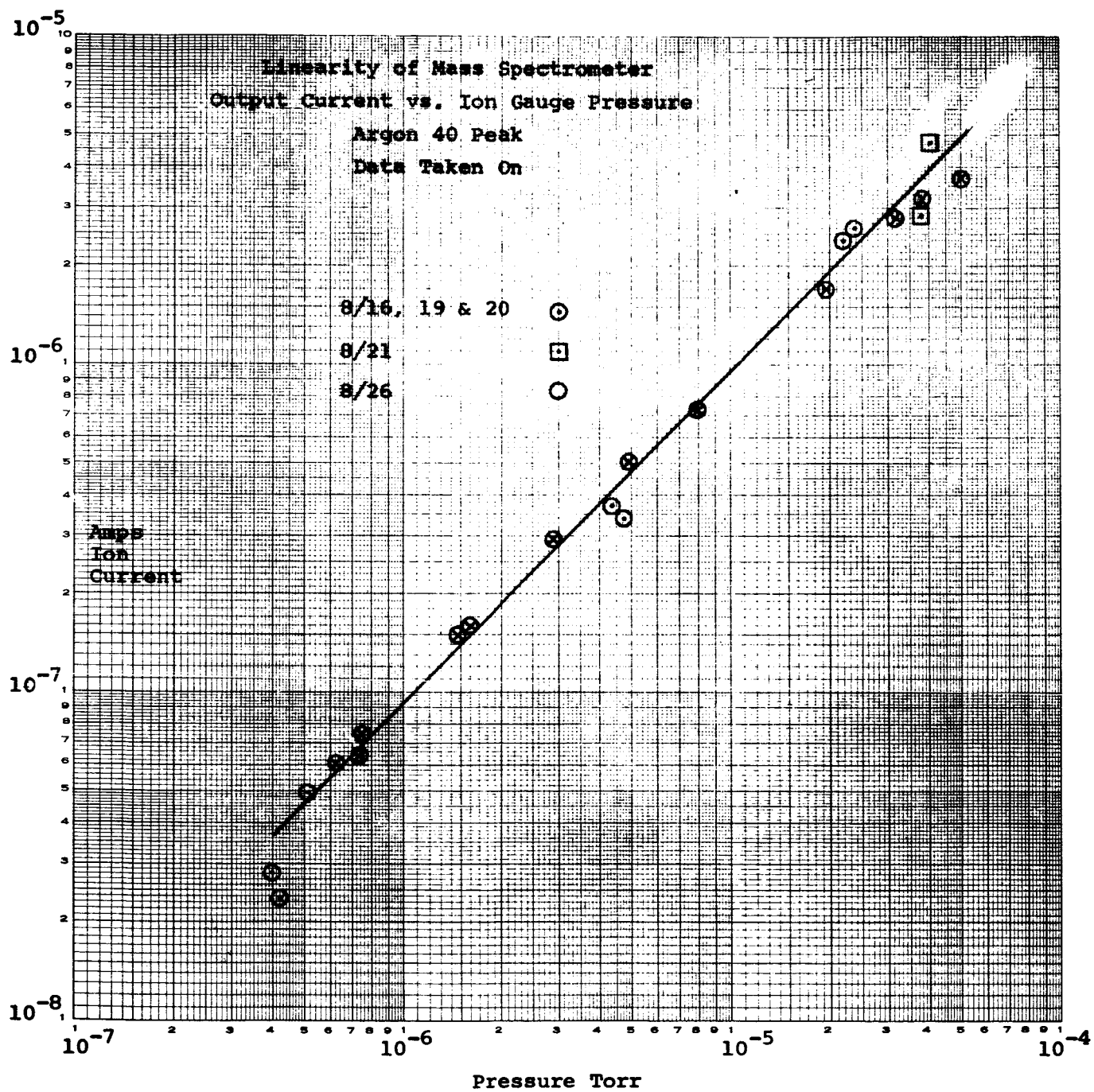

Spectrum Showing Mass Numbers Up to 200
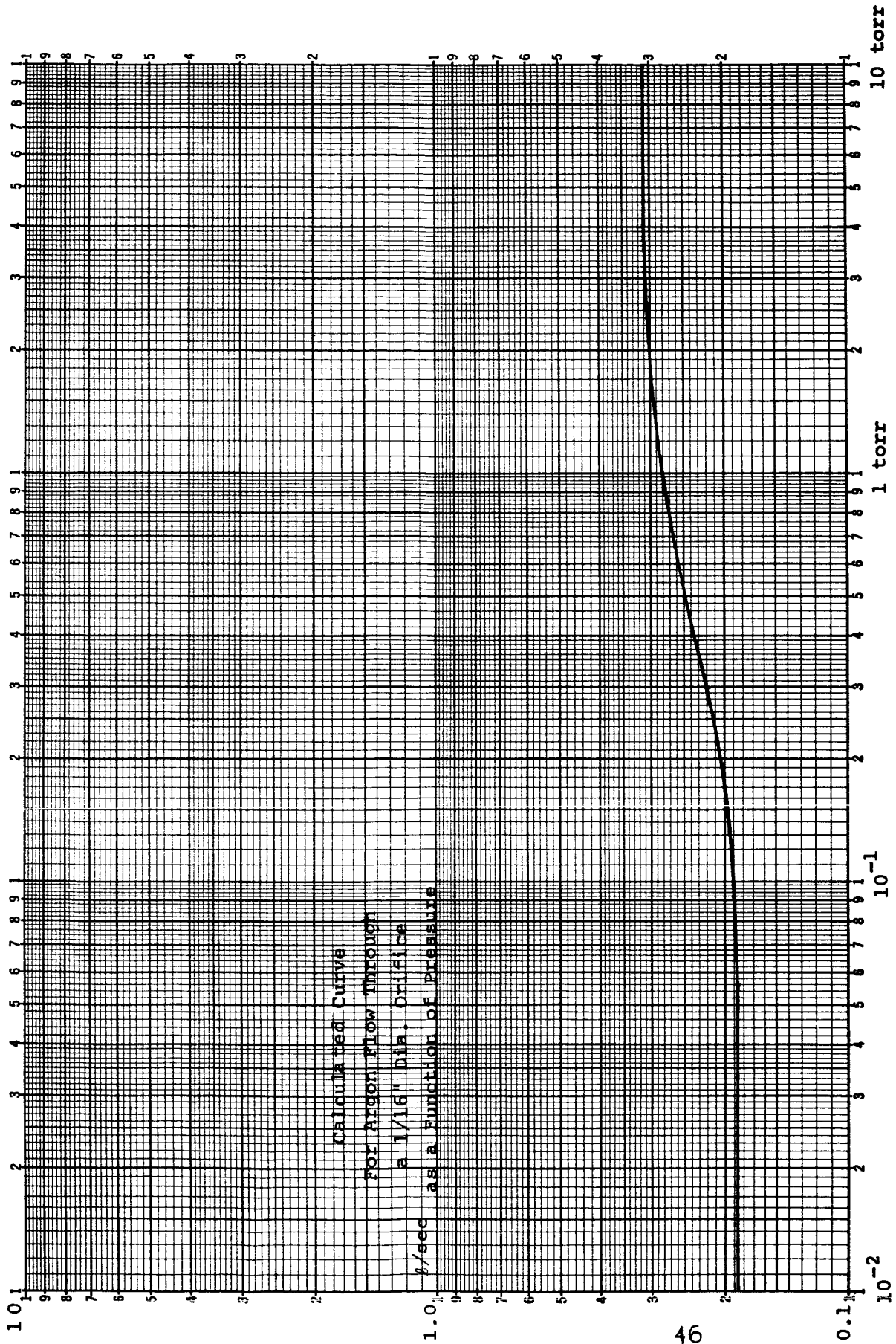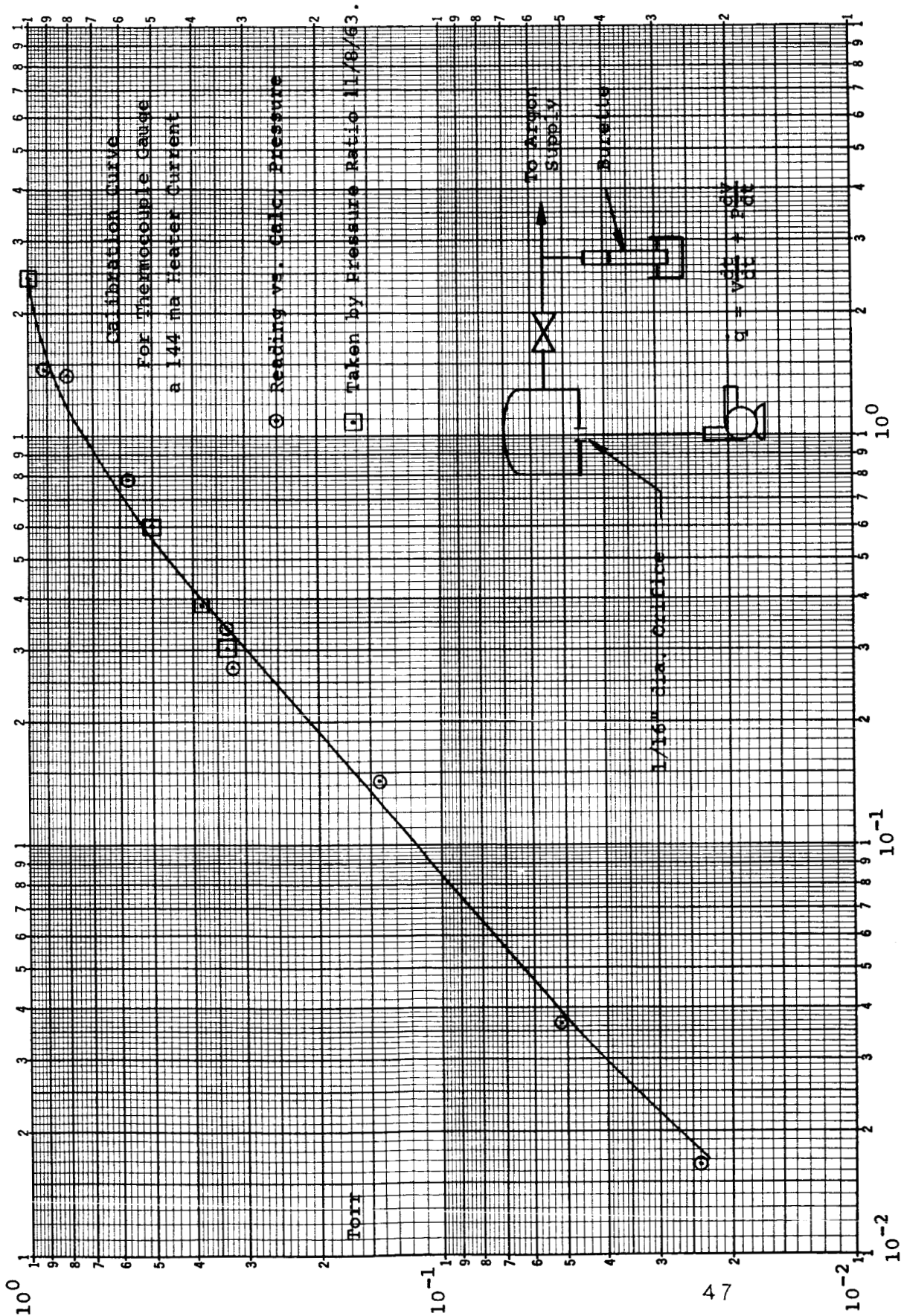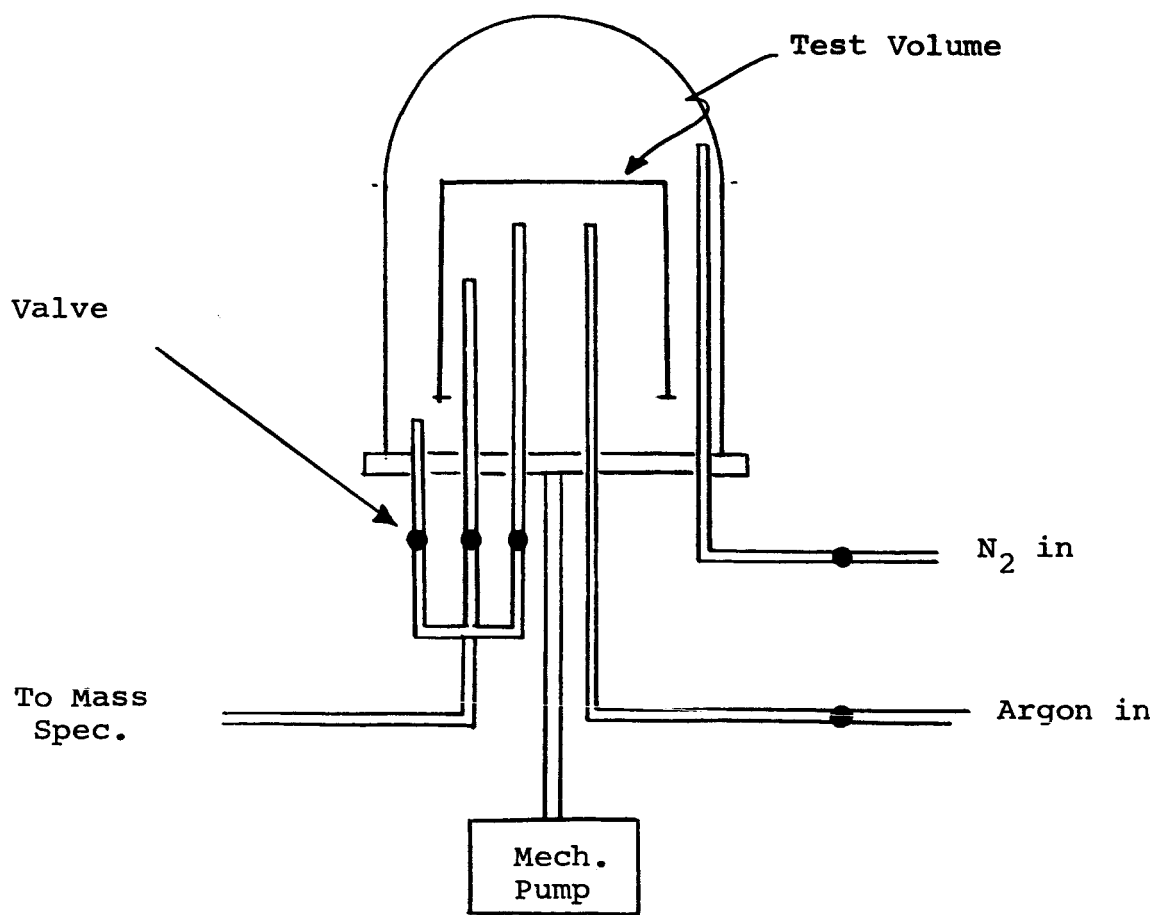
Fig. 3.4

Fig. 3.5

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Calculated Curve
For Argon Flow Through
a 1/16" Dia. Orifice
ℓ/sec as a Function of Pressure

Fig. 3.6

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Calibration Curve
For Thermocouple Gauge
a 144 ma Heater Current

⊙ Reading vs. Calc. Pressure
☐ Taken by Pressure Ratio 11/8/63.

To Argon Supply

Burette

$q = V\frac{dn}{dt} + n\frac{dV}{dt}$

1/16" dia. orifice

Pressure

Torr

47

Fig. 3.7

Test Volume

Valve

To Mass
Spec.

N_2 in

Argon in

Mech.
Pump

Schematic of Experimental Purge Setup

Figure 3.8

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Plot of Concentration
Ratio as a Function of
the Dimensionless
Parameter J*

$$J^* = \frac{\dot{q}x}{D^2}$$

$\dot{q}$ = gas flow rate in $\frac{\text{torr-liters}}{\text{sec}}$ at 25°C

D = diameter of crucible in inches

x = distance test location from crucible exit
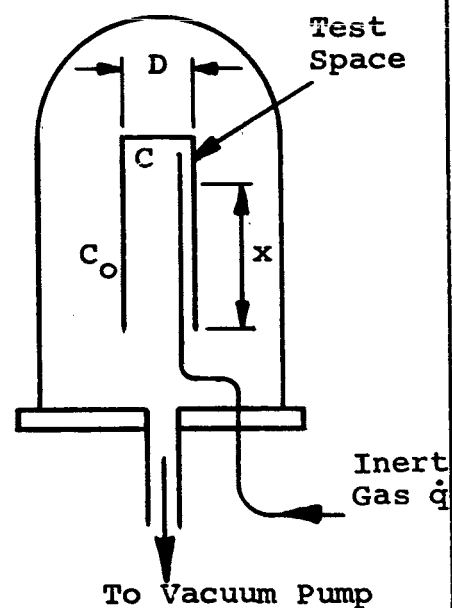
Test Space

To Vacuum Pump

Inert Gas $\dot{q}$

Fig. 3.9

4.0   SAMPLE ANALYSIS

4.0 SAMPLE ANALYSIS

Furnace Construction

Figs. 4.1 through 4.6 show the construction of the furnace. Six molybdenum radiation shields .010" thick were used to minimize the required heating power and to maintain uniform temperature in the crucible area. Two 1/8" diameter tantalum tubes were used to sample the gases. Both were located within the sample crucible. A third 1/8" diameter tantalum tube was used as a sample support as well as the argon inlet. Two platinum-platinum-rhodium thermocouples were located within the sample area to accurately measure temperature. These thermocouples generally measured within 15°F of one another. A tantalum crucible 1" diameter x 7" long covered the sample. One end of the crucible was welded closed to insure gas could only leave or enter from one end. A pair of Hevi-Duty heaters enclosed in an alumina ceramic provided the heating portion of the furnace.

The furnace worked satisfactorily up to temperatures of 1800°F. At 1800°F, the elements could not be relied upon to have a life longer than 300 hours. A furnace redesign is necessary for temperatures in excess of 1800°F.

The temperature of the thermocouples varied $\pm$ 4°F at set point. Since the thermal mass of the sample is considerably more than the thermocouple, the temperature variation of the sample should be even less.

Voltage Discharge

An experiment was performed to determine whether the operation of a furnace in the vacuum system and its associated voltage would be a serious problem.

A piece of 20" tungsten wire, .010" diameter, was put in the vacuum system and connected between two electrodes. The electrodes were such that the full voltage difference was applied across a gap of approximately 1". The bell jar was evacuated and the pressure

varied with a small leak of argon over the range 1 torr to .1 torr while 4 amps was passed through the wire. This raised the temperature of the wire to 2000°K. At this point, 60 volts was applied to the wire. No indication of an arc or discharge was noted.

From this experiment, it was concluded that 60 volts at the operating argon pressures would not cause any discharge problems. Actual furnace operation verified this.

Sample Exposure

Columbium - 1% zirconium samples were hung from a platinum wire supported by the argon inlet tube. The samples weighed approx. 7 grams and were 1/2" x 2" x .050" in dimensions. The test program required the samples be heated to 1500, 1850 and 2000°F for periods of one to 10 days. The temperature time plots for each sample are attached.

During the runs mass spectrums of the gas in the vicinity of the sample were made. Afterthe initial degassing of the sample and furnace, the analysis revealed only CO_2. The background level of the vacuum system indicated approximately the same level of CO_2. In one particular case, the gas analysis indicated $1.02 \ (10^{-10})$ amps CO_2 when the argon signal was $3 \ (10^{-6})$. The background level of CO_2 when the argon signal was immeasurable was $.93 \ (10^{-10})$. This difference is not significant. The background level probably was caused by holdup on the LN_2 trap. This level of CO_2 corresponds to a pressure of $.93 \ (10^{-8})$ torr which is the approximate vapor pressure of CO_2 at liquid nitrogen temperatures.

Analysis of the samples after exposure is not complete, but the results to date are summarized on Table 4.1.

It is difficult to interpret the results shown on the table. They are indicative of a rather pure atmosphere, equivalent to a vacuum of 10^{-6} to 10^{-7} torr. Further work is being performed at present by NASA, Lewis Research Center to complete the analysis.

The atmospheric pressure samples were enclosed in a quartz

tube 1" in diameter x 16" long. The sample was pumped down to approximately .05 torr by controlling the pressure with a small argon bleed. This pressure was maintained for approximately one hour. The system was then backfilled to 15" of mercury and then the tube was sealed off.

Fifteen inches of mercury of one-half an atmosphere was chosen to minimize the pressure differential during the heat exposure. At 2000°F, the pressure is between 3 and 4 times that at room temperature. During the heat exposure the tube is at some average temperature different than 2000°F. Therefore, the exact pressure is not known, but is probably between 1-2 atmospheres. The impurity level in the argon corresponds to 10 ppm at 380 torr. The volume of the tube is .206 liters. The total quantity of impurity is therefore 7.84 (10^{-4}) torr-liters which weighs 1.47 (10^{-3}) mg.

Adsorbed gas on the walls of the tube is another source for contamination. The amount of gas is dependent on the cleaning process. Typically, we might expect about 10^{-3} cm^3/cm^2. The tube had an area of 324 cm^2 or an expected quantity of gas of .3 torr-liters. The weight of this gas corresponds to 5.65 mg. The weight gain of the sample could be attributed to the gas adsorbed on the walls of the tube.

TABLE 4.1

Sample	Temp. of Exposure (°F)	Time of Exposure (hrs.)	Wgt. Gain (mg)	Vickers Hardness Test	O$_2$ Analysis (PPM)				Pump Speed ℓ/sec.	Pressure (Torr)
					1	2	7	8		
4	1500	239	0.0	108.6	830	810	810	820	2	.540
2	1500	23	-.08	120.1	1070	1070	740	740	2	.350
5	1500	24	.21						0	1 atm.
8	1750	164	.49						2	.410
3	1750	21.6	-.06	110.0	870	700	910	920	2	.540
6	1750	23.4	.38						0	1 atm.
13	2000	200							2	.560
9	2000	14	.83						2	.200
14	2000	26.8							0	1 atm.
Unexposed	0	0	--	--	950	950	950	950		

Vickers hardness test was performed with a 100 gram load.

53
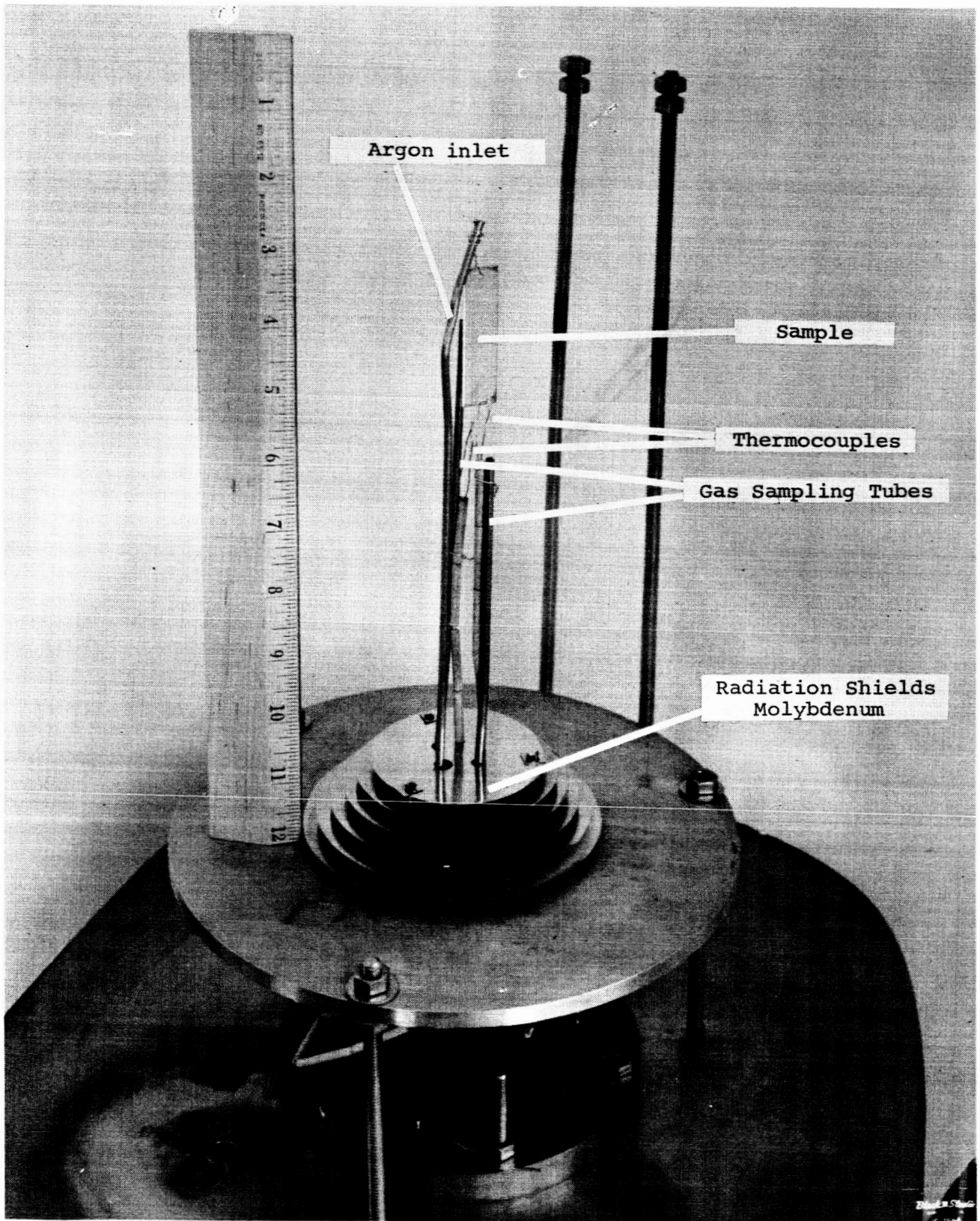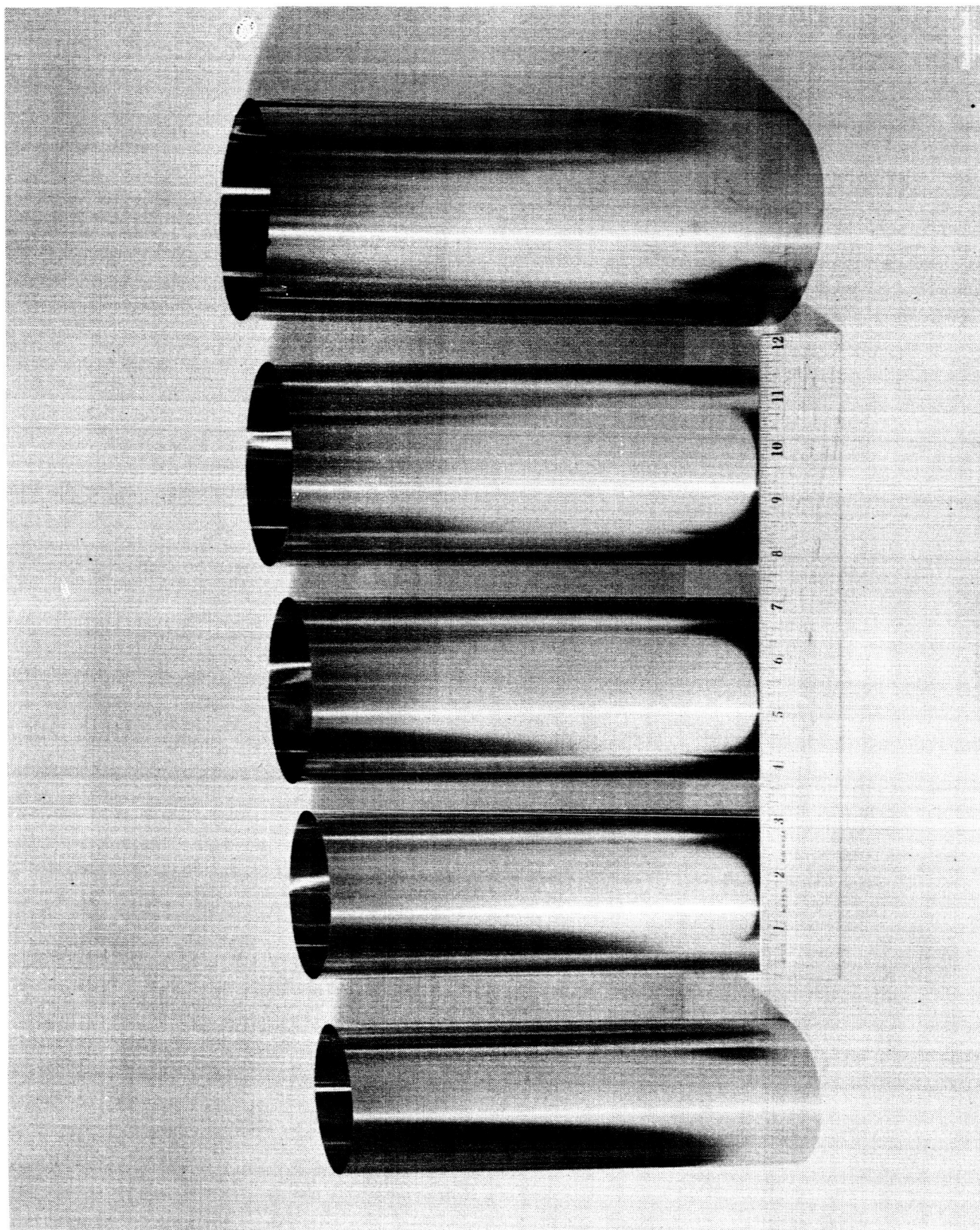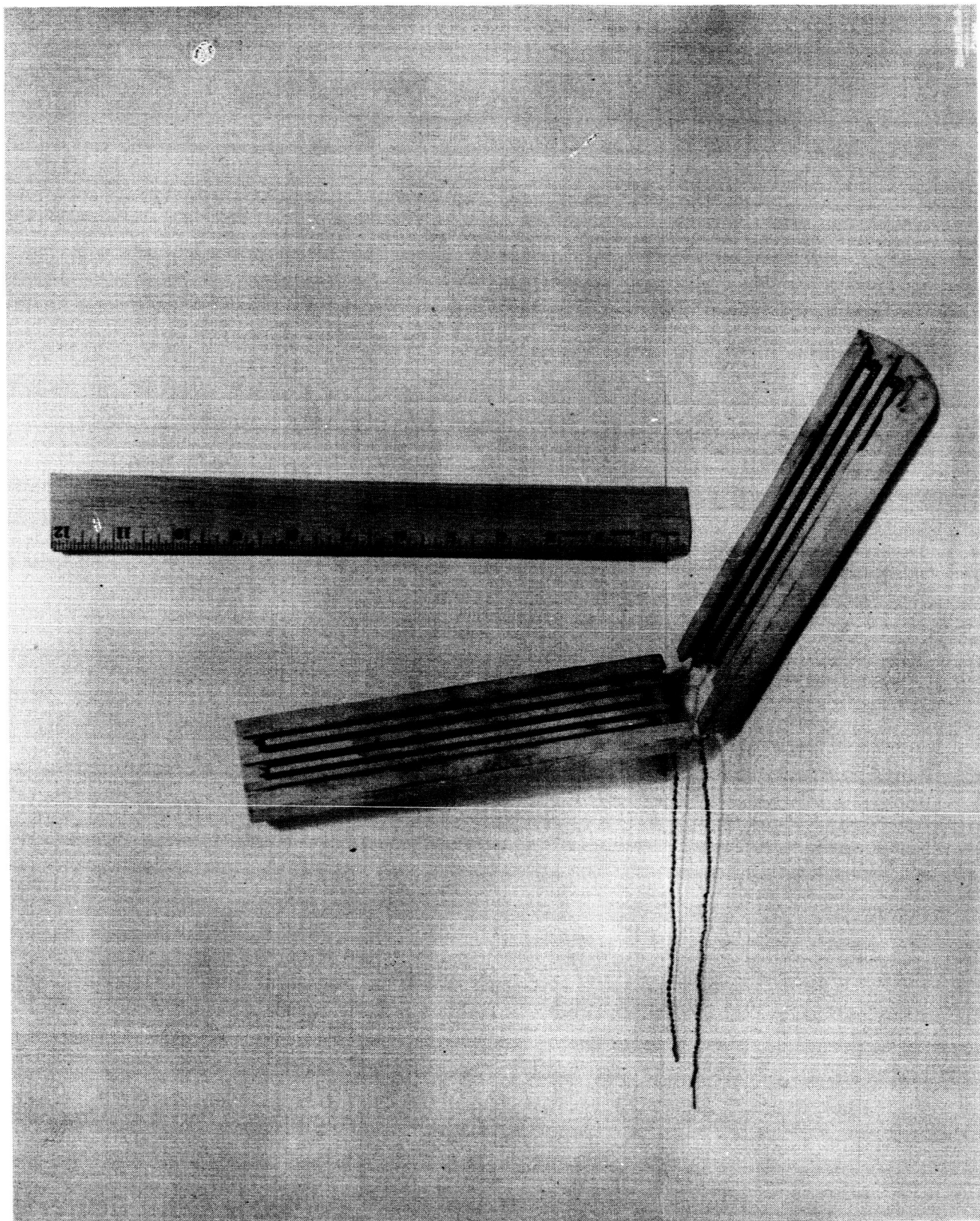
Sample Mounting Arrangement

Figure 4.1
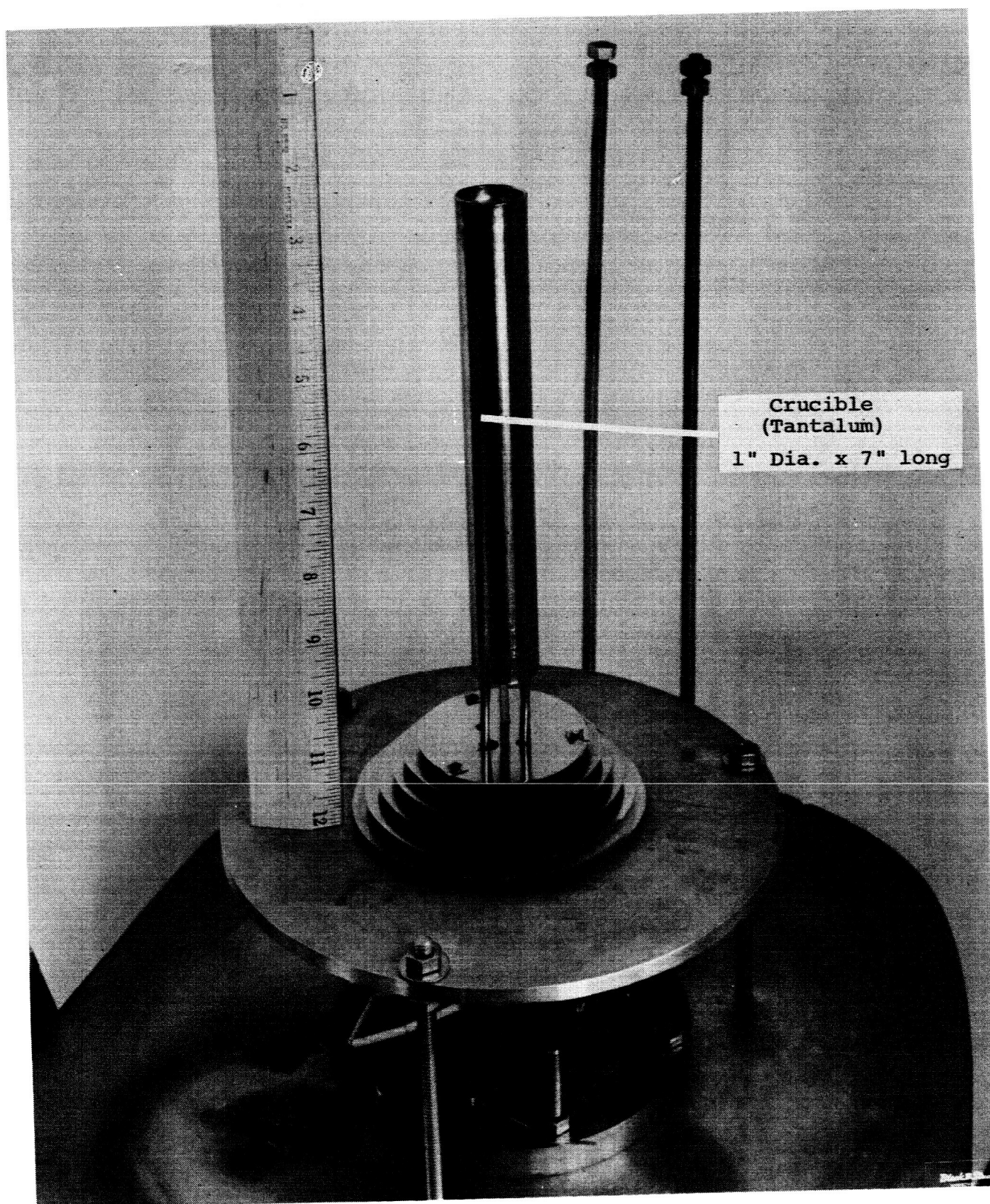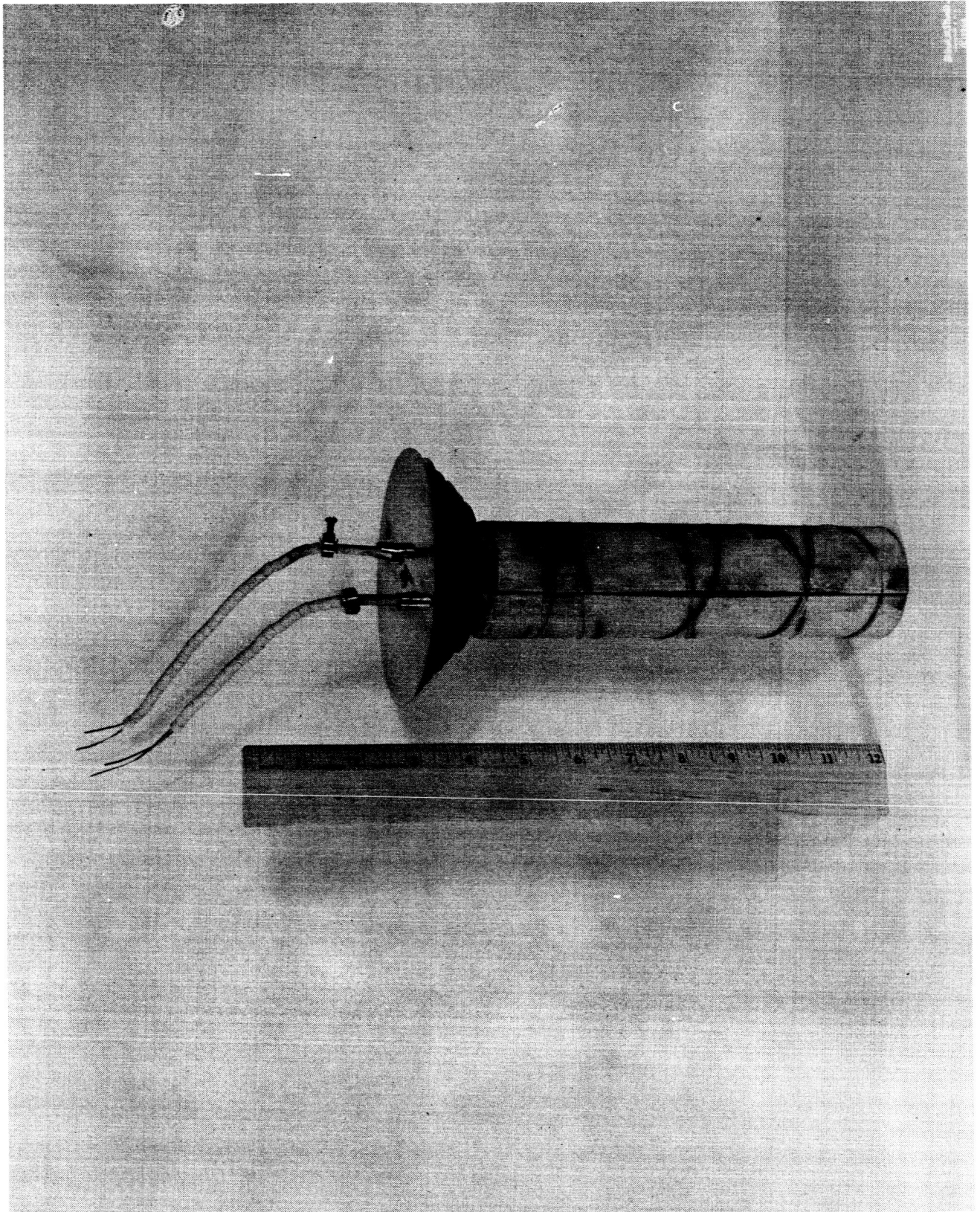
Crucible (Sample Enclosure)

Figure 4.2

Molybdenum Radiation Shields

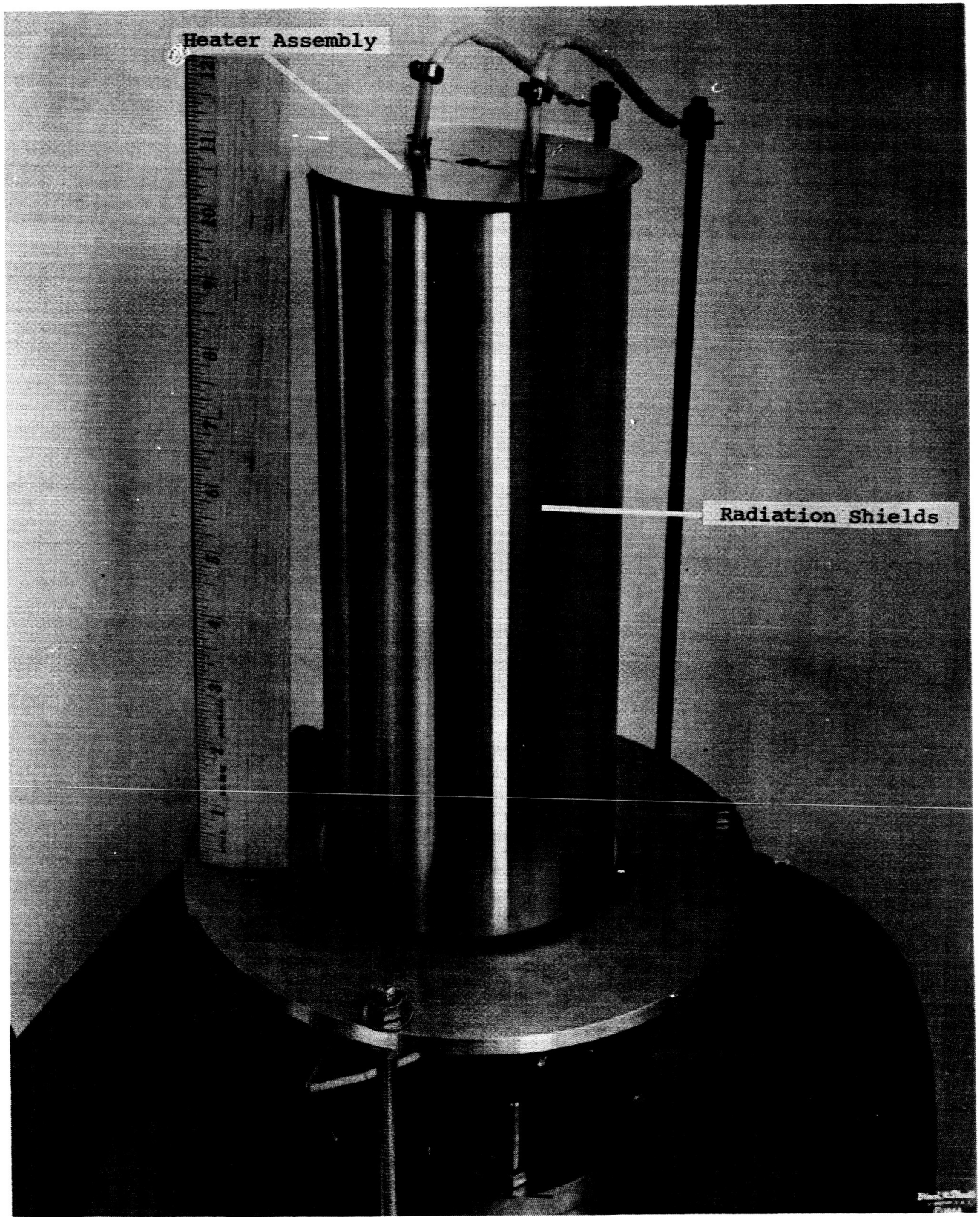Figure 4.3

Heater Unit

Figure 4.4

Heater Assembly

Figure 4.5

Furnace Assembly

Figure 4.6

Sample #2
Control temperature ± 5°F
Set Point 1500°F
Pressure .35 torr

60

Sample #5
Temperature 1500°F
Time 24 hours
Pressure 1/2 atm. Argon

CHR Alumel

Pressure ≈ 1 atm.

Power Off

1450 min. at 1500°F

No data available on rise due to
thermocouple slipping out of
position (Time is correct)

Hours

61

Sample # 6
Temperature 1750°F
Time 24 hours
Pressure 1/2 atm. Argon

CHR Alumel

Pressure ≈ 1 atm.

1400 min. at 1750°F   Power Off

Sample #3
Time 21.6 hours
Pressure .540 torr
Power Off

1300 min. at 1750°F

°F

1800

1600

1400

1200

1000

800

600

400

200

0   1   2   3   4   5   6   1   2

Hours
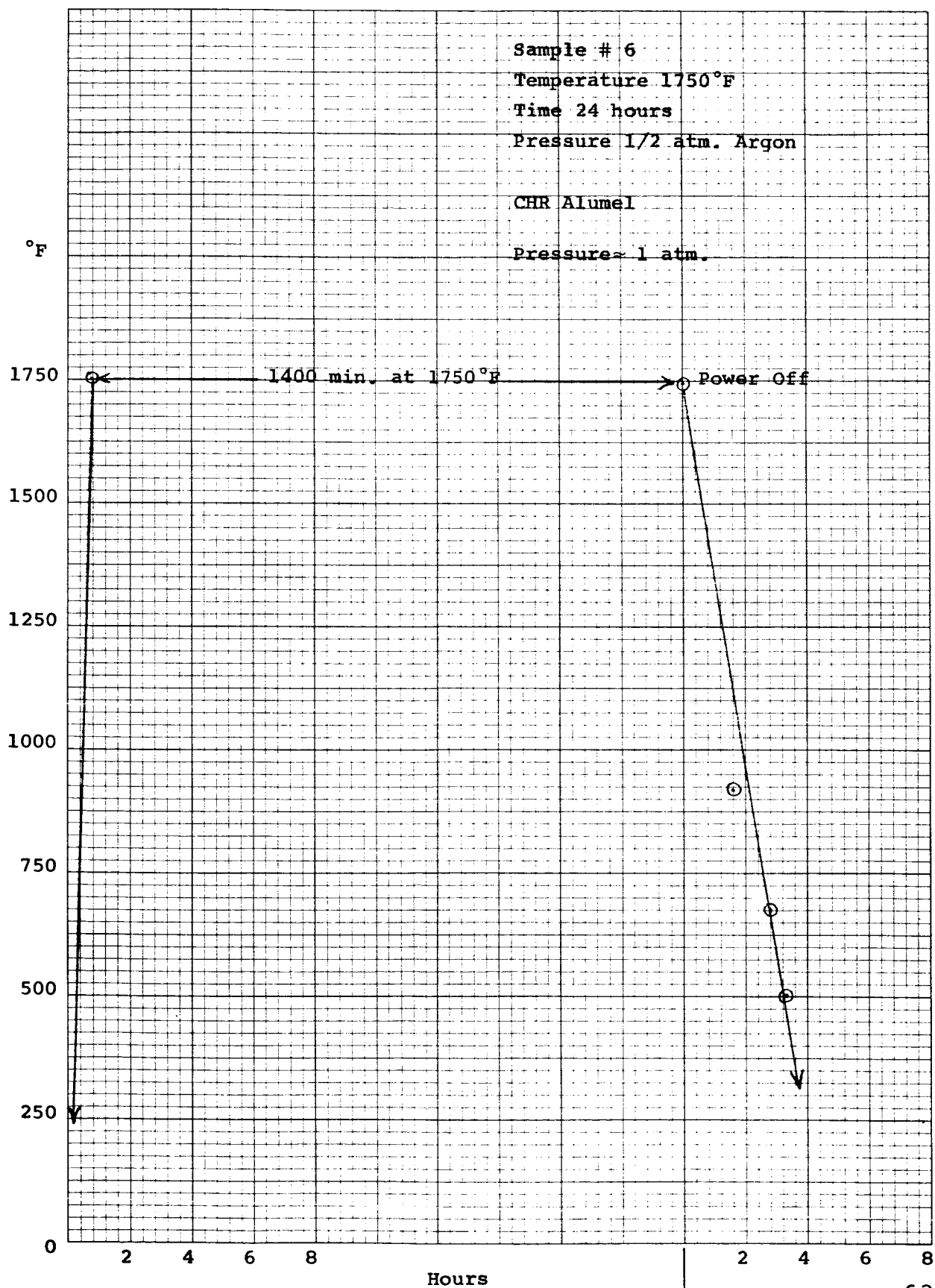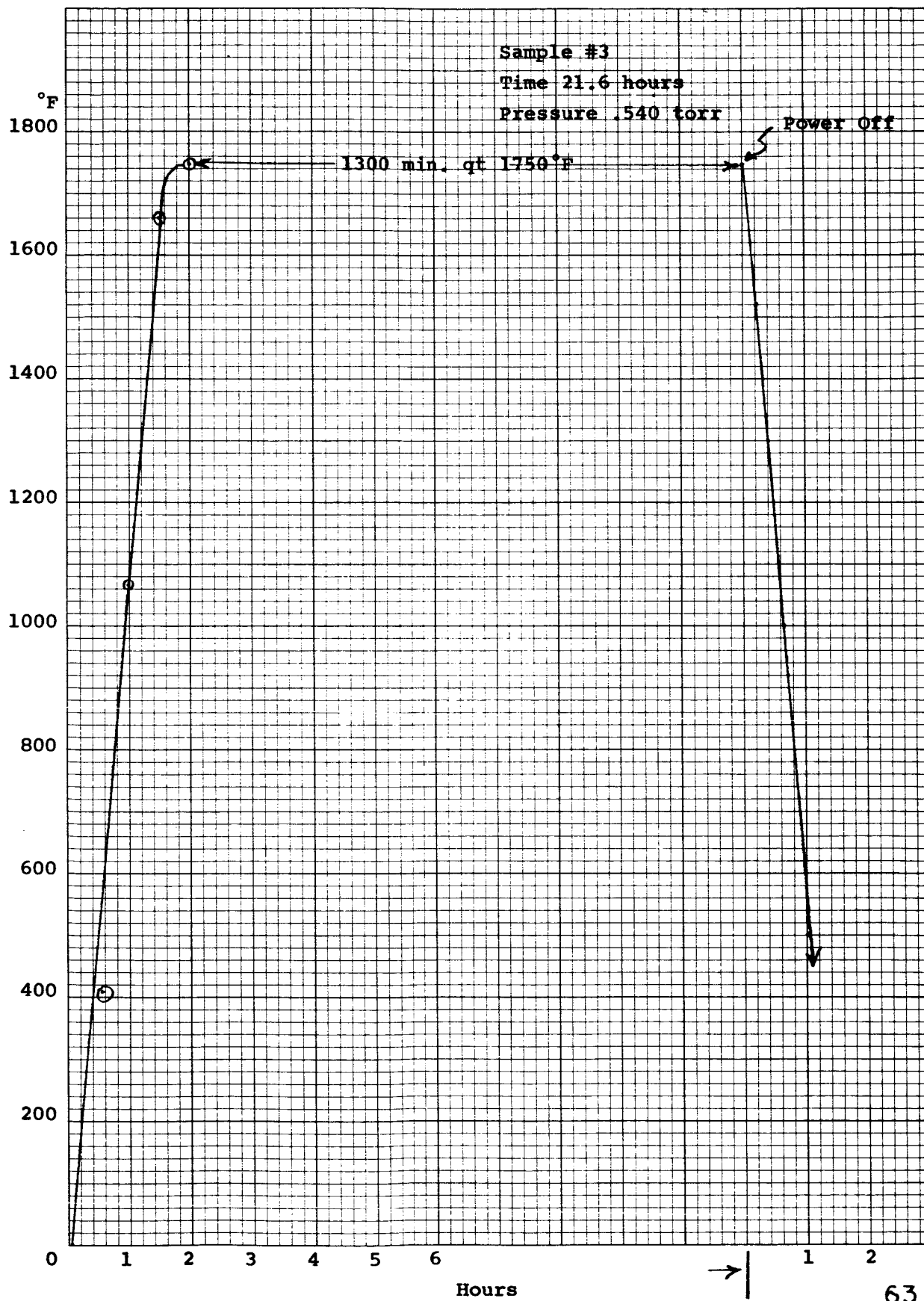
63

Sample #8
Temperature 1750°F
Time 164 hours
Pressure .410 torr

9840 min. at 1750°F   Power Off

°F

2100

1800

1500

1200

900

600

300

0   1   2   3   4   1   2   3   4

Hours

Sample #14
Temperature 2000°F
Time 24 hours

Pressure ≈ 1 atm.

1610 min. at 2000°F

Sample #9
Temperature 2000°F
Time 1 day
Pressure .200 (TCVC)

°F

2000   2000°F

1750

1500

1250

1000

750

500

250

0   2   4   6   8   10   20   22   24   26

Hours

Sample #13
Temperature 2000°F
Time 10 days
Pressure .560 torr

2000°F
200 hrs

1840°
533 hrs

2000

1800

1600

1400

1200

1000

800

600

400

200

0

Power Off

10 days at 1500°F

240

Hours

68